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CXVI.—*Note on Gynocardin and Gynocardase.*

By Charles Watson Moore and Frank Tutin.

The cyanogenetic glucoside gynocardin was first isolated by Power and Gornall (Proc., 1904, **20**, 137) from the seeds of *Gynocardia odorata*, R. Br., and has more recently been obtained by A. W. K. de Jong from the leaves of *Pangium edule*, Reinw. (*Rec. trav. chim.*, 1909, **28**, 24).

Power and Lees (Trans., 1905, **87**, 349) have shown that gynocardin possesses the formula $C_{13}H_{19}O_9N$, and that it undergoes hydrolysis according to the following equation:

$$C_{13}H_{19}O_9N + H_2O = C_6H_8O_4 + C_6H_{12}O_6 + HCN.$$

The last-mentioned investigators, however, found that, of the three hydrolytic products, only dextrose and hydrogen cyanide could be characterised, as the other product spontaneously resinified.

The present authors thought that some further information regarding the unknown hydrolytic product of gynocardin might be obtained by methylating gynocardinic acid (Power and Lees, *loc. cit.*) according to Purdie and Pitkeathly's method (Trans., 1899, **75**, 153), and subsequently hydrolysing the methylated product. Although the object in view has not been achieved, some new observations regarding gynocardin have been made which are considered worthy of record.

By the methylation of gynocardinic acid, a liquid *methyl* derivative was obtained which could be distilled without undergoing decomposition, and, on analysis, gave figures corresponding with the formula $C_{12}H_{14}O_4(OMe)_5\cdot CO_2Me$. The yield of this derivative was, however, small, and no definite hydrolytic product could be obtained from it.

Gynocardin has been found to possess feebly acidic properties. It is slightly acid to litmus, and yields with sodium ethoxide or sodium hydroxide a *sodium* derivative, $C_{13}H_{18}O_9NNa$.

It has been shown by Power and Lees (*loc. cit.*) that acids hydrolyse gynocardin only with difficulty, and the present authors thought that this might be owing to the fact that gynocardin was an α-glucoside, since E. F. Armstrong (*Proc. Roy. Soc.*, 1904, **74**, 188) has shown that such compounds undergo hydrolysis by means of dilute mineral acids more slowly than do their β-isomerides.

Quantitative experiments have now shown that, whereas gynocardin is rapidly hydrolysed by the enzyme gynocardase, which accompanies it in the seeds, it is comparatively indifferent towards emulsin. The converse of this is the case with amygdalin, this glucoside being only very slowly hydrolysed by gynocardase.

The behaviour of gynocardase towards salicin and maltose was then investigated, when it was ascertained that this enzyme caused only an extremely slow hydrolysis of the glucoside, but was absolutely without action on maltose. The effect of diastase on gynocardin was then examined, and it was observed that this enzyme was quite devoid of action on the glucoside in question, thus differing from emulsin, which does hydrolyse gynocardin, although only to a very minor extent.

When, however, the respective effects of gynocardase and emulsin on *l*-mandelonitrile glucoside were investigated, it was found that, in this case, the two enzymes possessed practically equal activity.

It is evident, therefore, that the glucoside, gynocardin, and the enzyme, gynocardase, must both belong to the β-series, notwithstanding the fact that emulsin is almost indifferent towards gynocardin, and that gynocardase has only a very slight action on amygdalin.

Quantitative experiments have also shown that the rate of hydrolysis of gynocardin by acids, although very considerably less than that of salicin, is actually greater than that of amygdalin.

It would appear, therefore, that gynocardin and gynocardase are analogous in their behaviour to phaseolunatin and its corresponding enzyme, which were originally assigned by Dunstan and Henry (*Proc. Roy. Soc.*, 1903, **72**, 285) to the α-series, but have quite recently been shown by H. E. Armstrong and E. Horton (*ibid.*, 1910, **28**, *B*, 349) to belong to the β-series.

The fact that the enzyme from *Phaseolus lunatus* seeds is quite active towards *l*-mandelonitrile glucoside, whilst it exerts only a very minor action on amygdalin, was attributed by Armstrong and Horton (*loc. cit.*) to the inhibiting action of the second glucose molecule in the last-mentioned compound. Gynocardase, however, although behaving quite analogously to phaseolunatase with respect to amygdalin and *l*-mandelonitrile glucoside, only causes an extremely slow hydrolysis of salicin. It is evident, therefore, that the nature of the non-glucose part of the molecule of a glucoside may also exert a considerable influence with regard to the susceptibility of such a compound to the action of enzymes.

EXPERIMENTAL

Methylation of Gynocardinic Acid.

Gynocardinic acid was prepared by the action of hot barium hydroxide on gynocardin, when ammonia is evolved and barium gynocardinate formed (Power and Lees, *loc. cit.*). The barium gynocardinate thus obtained is a readily soluble salt, from which the gynocardinic acid may be prepared by exactly precipitating the barium with sulphuric acid. It was observed by the present authors that when a considerable excess of barium hydroxide is employed in the hydrolysis a very sparingly soluble crystalline double compound of barium gynocardinate and barium hydroxide separates, but this was not further investigated.

Twenty grams of gynocardinic acid were methylated by means of methyl iodide and dry silver oxide according to Purdie and Pitkeathly's method (*loc. cit.*). The methylation was first carried out in methyl alcohol solution, and was repeated under these conditions until the product was soluble in methyl iodide, after which further methylation was effected in methyl iodide solution, the treatment being continued until there was no further reaction on boiling with dry silver oxide. The methylated product was removed from the reaction mixture by means of ether. It formed a syrup, which showed no signs of crystallising. When distilled under diminished pressure, a definite fraction boiling at 220°/15 mm. was obtained, which formed a viscid liquid at the ordinary temperature:

0·1642 gave 0·3170 CO_2 and 0·1145 H_2O. C=52·6; H=7·7.
$C_{19}H_{32}O_{11}$ requires C=52·3; H=7·3 per cent.

A determination of the number of methoxyl groups by Perkin's modification of Zeisel's method gave the following result:

0·1880 gave 0·6010 AgI. OMe=42·2.
$C_{13}H_{14}O_5(OMe)_6$ requires OMe=42·6 per cent.

This substance is therefore a *methyl pentamethylgynocardinate*, $C_{12}H_{14}O_4(OMe)_5{\cdot}CO_2Me$, and must therefore still contain two hydroxyl groups, since Power and Lees have shown that gynocardin yields a hepta-acetyl derivative. In the endeavour to obtain a fully methylated product, a small quantity of the ester was heated with methyl iodide and dry silver oxide for some hours at 100° in a sealed tube, but the product gave practically the same results on analysis as before this treatment.

On boiling methyl pentamethvlgynocardinate with dilute sulphuric acid, it was completely decomposed, nothing but brown, resinous products resulting.

Sodium Derivative of Gynocardin, $C_{13}H_{18}O_9NNa$.

As already mentioned, gynocardin possesses feebly acidic properties, in virtue of which it is able to form derivatives with the alkali metals. On adding excess of sodium ethoxide or aqueous sodium hydroxide to an ethyl-alcoholic solution of gynocardin, a white precipitate is produced, readily soluble in water or methyl alcohol, but sparingly so in ethyl alcohol:

0·4140 gave 0·0635 Na_2CO_3. Na = 6·6.

$C_{13}H_{18}O_9NNa$ requires Na = 6·5 per cent.

Attempts to prepare methyl gynocardin from this *sodium* derivative were unsuccessful.

Action of Gynocardase and Emulsin on Gynocardin and other Glucosides.

As stated above, gynocardin is but slowly hydrolysed by boiling dilute mineral acids, although this change is rapidly effected by means of the enzyme, gynocardase, which was obtained from *Gynocardia* seeds by Power and Lees (*loc. cit.*). Amygdalin, on the other hand, is only very slowly acted upon by gynocardase, the action requiring about twelve hours before any benzaldehyde and hydrogen cyanide can be detected. The effect of gynocardase and emulsin on gynocardin and amygdalin has therefore been examined quantitatively. In each case 0·5 gram of the glucoside was dissolved in 50 c.c. of water and 0·2 gram of enzyme added, the mixture being allowed to remain for thirty minutes at 25°. The resulting hydrogen cyanide was then removed by a current of steam, and estimated by titration with silver nitrate in presence of a little sodium chloride, in the usual manner.

The results of these experiments are shown in the following table:

Enzyme.	Glucoside.	Volume of $N/10$-$AgNO_3$ required.	Percentage of glucoside hydrolysed.
Gynocardase	Gynocardin	4·0 c.c.	57·6
Gynocardase	Amygdalin	$<0·1$,,	none measurable
Emulsin	Gynocardin	$<0·1$,,	,, ,,
Emulsin	Amygdalin	4·8 ,,	88·1

The effect of the two enzymes in question on salicin was also investigated, and for this purpose one gram of the glucoside was dissolved in 100 c.c. of water, and 0·5 gram of the respective enzyme added. The mixture was then allowed to remain at 20° for thirty minutes, after which the saligenin formed was isolated by means of ether, and weighed. The results obtained were as follows:

One gram of salicin, on treatment with gynocardase, gave 0·0050 of saligenin. Percentage of glucoside hydrolysed = 1·2.

One gram of salicin, on treatment with emulsin, gave 0·2100 of saligenin. Percentage of glucoside hydrolysed = 48·4.

The relative activity of emulsin and gynocardase towards *l*-mandelonitrile glucoside was ascertained in the following manner. A sufficient supply of the pure glucoside not being available, an extract of the bark of *Prunus serotina*, Ehrhart, was employed, as this has been shown to contain *l*-mandelonitrile glucoside (Power and Moore, Trans., 1909, **95**, 243). One hundred grams of the finely powdered bark were brought into 5 litres of boiling water, the mixture boiled for some time, and then filtered. The filtrate was evaporated under diminished pressure to 200 c.c., and then divided into two equal portions, to one of which 0·4 gram of gynocardase was added, and to the other the same amount of emulsin. Each of the mixtures was then kept for thirty minutes, after which the liberated hydrogen cyanide was estimated as before described. It was then found that the portion treated with gynocardase required, on titration, 1·6 c.c. of $N/10$-silver nitrate solution to produce a permanent turbidity, whilst the other mixture, which contained emulsin, required an almost identical amount, namely, 1·55 c.c.

Acid Hydrolysis of Gynocardin, Amygdalin, and Salicin.

The respective rates of hydrolysis by acids of gynocardin, amygdalin, and salicin were estimated quantitatively, as follows.

Equimolecular quantities of the three glucosides (1·00, 1·32, and 0·80 grams respectively) were boiled with 200 c.c. of a 2 per cent. aqueous solution of sulphuric acid. In the case of the two cyanogenetic compounds, steam was passed through the mixture for two hours, the liquid being maintained at practically a constant volume, after which the hydrogen cyanide in the distillate was estimated in the usual manner. In the case of salicin the mixture was heated for one hour in a flask attached to a reflux condenser, and the saligenin then isolated by means of ether, and weighed. It was thus found that, under analogous conditions, the extent to which these three glucosides were hydrolysed was as follows: Gynocardin, 6·5 per cent.; amygdalin, 5·0 per cent.; salicin, 78·7 per cent.

A quantity of gynocardin was dissolved in water, and diastase added, but, even after ten days, no hydrogen cyanide was developed. Similarly, on treating maltose with gynocardase for twenty-four hours, no change occurred, for, on subsequently converting the sugar into osazone, the product was found to consist solely of maltosazone.

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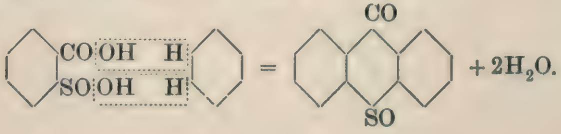
CXVII.—*New Syntheses of Thioxanthone and its Derivatives.*

By Eric Gordon Davis and Samuel Smiles.

The experiments described in this paper were the outcome of a desire to study certain of the oxidation products of thioxanthene; but with this object in view it was necessary to obtain a considerable quantity of that substance. The preparation of thioxanthene by the method hitherto followed is somewhat tedious, since it involves the isolation of certain intermediate products, and the yield obtained leaves much room for improvement in the process. This synthesis of thioxanthene was devised by Graebe and Schulthess (*Annalen*, 1891, **263**, 1); it consists in the removal of the elements of water from *o*-phenylthiolbenzoic acid, $C_6H_5\cdot S\cdot C_6H_4\cdot CO_2H$, by means of hot sulphuric acid. The yields of thioxanthone obtained from this reaction are good, but the crucial point of the synthesis is the production of the carboxylic acid. Graebe and Schulthess (*loc. cit.*) prepared the latter substance by the interaction of phenyl mercaptan and the *o*-diazonium chloride of benzoic acid in alkaline solution; but since the introduction of *o*-thiolbenzoic acid as a cheap commercial product (Kalle & Co., D.R.-P. 205450 of 1908), F. Mayer (*Ber.*, 1909, **42**, 1134) has improved Graebe and Schulthess's process by heating the methyl ester of this acid with sodium ethoxide, bromobenzene, and copper powder to 160° for four hours. The yield of *o*-phenylthiolbenzoic acid obtained by this method was about 50 per cent.

In order to avoid the isolation of these intermediate products, we have employed *o*-carboxybenzenesulphinic acid, which is readily obtained from anthranilic acid by the process devised by Gattermann (*Ber.*, 1899, **32**, 1144), or by the reduction of the dichloride of *o*-carboxybenzenesulphonyl chloride. In previous papers (Smiles and Le Rossignol, Trans., 1906, **89**, 700) it has been shown that sulphinic acids readily condense with aromatic compounds in presence of dehydrating agents, yielding the corresponding sulphoxides, and it has now been found that the sulphinic acid in question undergoes this reaction. If, however, the condensation is carried out in the presence of hot concentrated sulphuric acid, the carboxyl group also takes part in the reaction, and the thioxanthone is immediately produced, for example, with benzene:

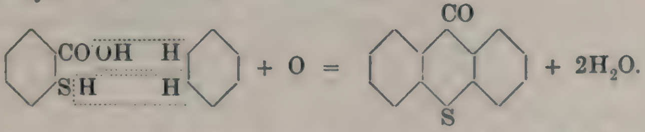


It may, however, be observed that, when dissolved in concentrated sulphuric acid, the sulphoxides are not stable in presence of a sulphinic acid, being reduced by the latter to sulphides (compare Smiles and Le Rossignol, Trans., 1906, **89**, 707); hence the product which is isolated is not the sulphoxide formulated in the above equation, but is thioxanthone itself. In the case of the condensation of *o*-carboxybenzenesulphinic acid with benzene, the yield of thioxanthone is about 60 per cent. of that required by theory, and the fact that it does not more closely approach the theoretical is probably due to this instability of the sulphoxide. There is no doubt that the reduction of the sulphoxide takes place partly at the expense of the uncombined sulphinic acid, and the latter, being converted into the sulphonic acid, would then be prevented from undergoing the required condensation. In order to avoid this loss, we endeavoured to find a means by which the formation of the sulphoxide would be avoided.

Stenhouse (*Annalen*, 1869, **149**, 250; also Erlenmeyer and Lisenko, *Jahresber.*, 1861, 590) has shown that the mercaptans are readily oxidised by concentrated sulphuric acid, being converted into disulphides, thus:

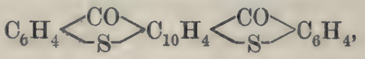
$$2R\cdot SH + O = R\cdot S\cdot SR + H_2O.$$

Nothing is at present known of the mechanism of this reaction, and it seems to have been tacitly assumed that hydrogen is simultaneously removed by oxidation from two molecules of the mercaptan; there is, however, the alternative explanation that an oxygen derivative of the mercaptan is first formed, which then unites with the second molecule, forming the disulphide and one molecular proportion of water. The probability that, if the latter alternative is correct, this oxygen derivative of the mercaptan might be made to condense with aromatic nuclei justified the attempt to obtain thioxanthone by the interaction of *o*-thiolbenzoic acid and benzene in the presence of hot concentrated sulphuric acid. The result was successful, the yield under favourable conditions being as high as 90 per cent. of the theoretical. The reaction which takes place may be formulated as follows:



Experiments conducted with a wide range of material indicate that this method of preparing derivatives of thioxanthone is of general application; for, as might be anticipated from the behaviour of the parent substance, the majority of simple benzene derivatives furnish the corresponding thioxanthones.

Also, naphthalene and its derivatives yield the naphthathioxanthones, but here the reaction may proceed a stage further than with the simpler benzene derivatives. It will be observed that the conditions under which the reaction has been carried out are such that the *o*-thiolbenzoic acid, being dissolved in the concentrated acid, is always in excess of the less soluble naphthalene derivative which is gradually added during the progress of the reaction, and there is thus formed the bisthioxanthone:



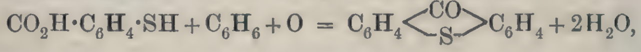
$$C_6H_4{<}\substack{CO\\S}{>}C_{10}H_4{<}\substack{CO\\S}{>}C_6H_4,$$

by the interaction of two molecules of *o*-thiolbenzoic acid and one of naphthalene. We have not yet observed the formation of the bisthioxanthones with benzene or its derivatives, and it is therefore probable that in the above naphthalene compounds the thioxanthone arrangements are attached to different cyclic systems.

A few words may be said on the interesting question of the mechanism of this reaction. It is clear from the reaction discovered by Stenhouse, to which reference has already been made, and from that described in the present paper, that in concentrated sulphuric acid solution the *o*-thiolbenzoic residue, $CO_2H \cdot C_6H_4 \cdot S \cdot$, may be united at will either to a second *o*-thiolbenzoic group* or to an aromatic complex. It is also evident that in presence of an aromatic compound the latter course is preferred.

According to common hypothesis, these reactions would proceed as follows:

(*a*) $2CO_2H \cdot C_6H_4 \cdot SH + O = (CO_2H \cdot C_6H_4 \cdot S)_2 + H_2O.$

(*b*) 

$$CO_2H \cdot C_6H_4 \cdot SH + C_6H_6 + O = C_6H_4{<}\substack{CO\\S}{>}C_6H_4 + 2H_2O,$$

the hydrogen atoms of the mercaptan or aromatic complex being simultaneously removed by direct oxidation; but we consider that the facts which are above outlined render this hypothesis untenable, and chiefly for the following reasons.

(1) The thiol hydrogen atom of the mercaptans is very easily removed by oxidation (for example, by iodine in aqueous solution, or by air in alkaline solution), and far more easily removed by oxidation than hydrogen of the aromatic complex. Hence it appears that if this hypothesis be correct, the mercaptans should be almost entirely converted into disulphides whether the less readily oxidised aromatic compound be present or not. This, however, is not the case; in the examples now dealt with, only a

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* *o*-Thiolbenzoic acid here behaves like other mercaptans, and is readily oxidised by cold concentrated sulphuric acid to dithiosalicylic acid, sulphurous acid being evolved.

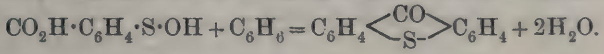
very small quantity of *dithiosalicylic acid* is formed, the bulk of the product—about 90 per cent.—being thioxanthone.

(2) It may be observed that the formation of thioxanthone proceeds to a certain extent in sulphuric acid at about 20°, and it is difficult to imagine that aromatic hydrogen should be directly attacked by oxygen from that reagent under such conditions.

For these reasons we have rejected this hypothesis, and as an alternative adopt the only other which affords an adequate explanation: that the mercaptans are first oxidised by the sulphuric acid to an unstable oxygen derivative, which then unites with the aromatic complex or a second molecule of the mercaptan, water being eliminated under the influence of the condensing reagent. Further, adopting this explanation, it is evident that this intermediate compound must be one of the sulphoxylic acids which have so often been assumed by chemists to be formed in the reactions of the lower oxidation products of organic sulphur compounds. The reactions in question would then be represented as follows:

(1) $CO_2H\cdot C_6H_4\cdot SH + H_2SO_4 = CO_2H\cdot C_6H_4\cdot S\cdot OH + H_2SO_3$.

(*a*) $CO_2H\cdot C_6H_4\cdot S\cdot OH + HS\cdot C_6H_4\cdot CO_2H = (CO_2H\cdot C_6H_4\cdot S)_2 + H_2O$.*

(*b*) 
$CO_2H\cdot C_6H_4\cdot S\cdot OH + C_6H_6 = C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{S-}{>}C_6H_4 + 2H_2O$.

It is true that no direct proof of the existence of these sulphoxylic acids has yet been adduced either in these reactions or in any others in which they have been postulated, and in many other cases the evidence brought forward to warrant the assumption is very slender and open to other interpretation. However, in the present case there appears to us to be no satisfactory alternative. Further, it might be questioned whether the sulphoxylic acid, even if it were formed, would undergo condensation with aromatic compounds, but in answer to this it may be observed that it has been already shown that hydroxyl attached to partly oxidised sulphur behaves in this manner (Smiles and Le Rossignol, Trans., 1906, **89**, 696; 1908, **93**, 745); thus aromatic sulphinic acids and sulphoxide salts may be condensed in ice-cold sulphuric acid with aromatic compounds, giving triarylsulphonium salts, and even sulphur dioxide exhibits this reaction.

In summing up the case for the existence of the sulphoxylic acid in the present reactions, it may be said that the alternative explanation is untenable, that all the available evidence is in its favour, and, whilst this is only of an indirect nature, there is none in contradiction.

With the view of throwing further light on this question, the reactions of the mercaptans and disulphides in concentrated sulphuric acid are now being studied, and attempts are being made to obtain derivatives of these sulphoxylic acids.

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* Considerable evidence may be adduced to show that, in concentrated sulphuric acid, this reaction is reversible; the question is at present under investigation.

In the following pages are described the more important of the derivatives of thioxanthone which have been prepared by this method, and it may be observed that at present the position of the substituents in the aromatic nuclei is uncertain. In view of the experiments which are being made by F. Mayer on other syntheses of these substances, we do not propose to follow up this question in detail.

EXPERIMENTAL.

With the object of synthesising thioxanthone from *o*-carboxybenzenesulphinic acid, it was necessary to obtain this acid in some quantity. It has already been prepared by Gattermann (*Ber.*, 1899, **32**, 1144) by the interaction of *o*-carboxybenzenediazonium sulphate and sulphurous acid in the presence of copper powder; but in order to find the best method of preparing the acid, experiments were made with the alternative method of reducing *o*-carboxybenzenesulphonyl chloride. Preliminary experiments were made with the less expensive meta-derivative.

m-*Carboxybenzenesulphinic Acid.*

The dichloride of *m*-carboxybenzenesulphonic acid was prepared according to the method described by Limpricht and Uslar (*Annalen*, 1857, **102**, 250), and it was reduced to the sulphinic acid by the following process. A saturated aqueous solution of sodium sulphite was warmed on the water-bath, and the chloride was gradually added to this, the mixture being constantly shaken and kept alkaline during the course of the reaction. When all the chloride had dissolved, the contents of the flask were cooled, and then carefully acidified with concentrated sulphuric acid. The greater part of the sulphinic acid was precipitated during this process, but it was completely extracted from the mixture with ether. After the ethereal solution had been dried, it was distilled, and the residue was washed with benzene and recrystallised from hot water. Thirty-four grams of sulphinic acid were obtained from 44 grams of the chloride. A sample which had been dried in a vacuous desiccator was analysed:

0·2405 gave 0·3974 CO_2 and 0·0657 H_2O. $C=45·1$; $H=3·04$.

0·2449 ,, 0·3075 $BaSO_4$. $S=17·25$.

1·2502 required 13·1 c.c. of 1·01*N*-KOH for neutralisation.

Equivalent = 94·7.

$C_7H_6O_4S$ requires $C=45·17$; $H=3·22$; $S=17·2$ per cent.

Equivalent = 93.

When heated, the acid melts with profound decomposition, and the temperature at which this takes place depends somewhat on the rapidity of heating; under ordinary conditions it lies between 195° and 200°. Gattermann (*Ber.*, 1899, **32**, 1144) gives 197—198° as the melting point. The substance is soluble in cold water and most organic media. That the compound is a sulphinic acid is shown by the production of a blue colour when treated with phenetole in concentrated sulphuric acid, and by the fact that it yields the normal type of product when treated with nitrous acid.

Action of Nitrous Acid.—A slight excess of sodium nitrite was dissolved in an aqueous solution of the sodium salt of the acid. Dilute sulphuric acid was then slowly added to the cooled mixture, when the required oximino-derivative immediately separated in the crystalline state. The yield was almost quantitative. The substance was collected, well washed with water, and finally crystallised from that medium containing a little nitrous acid:

0·7768 gave 26·1 c.c. N_2 at 18° and 748 mm. N = 3·9.

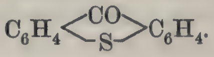
$C_{14}H_{11}O_9NS_2$ requires N = 3·5 per cent.

Dicarboxybenzenesulphohydroximic acid forms colourless prisms, which are soluble in hot water, and are slightly decomposed thereby. It is resolved into the components by cold aqueous alkali hydroxide, and on being gently warmed it evolves oxides of nitrogen.

o-Carboxybenzenesulphinic Acid.

The stable dichloride (Remsen and Dohme, *Amer. Chem. J.*, 1889, **11**, 340) of *o*-carboxybenzenesulphonic acid was prepared by the action of phosphorus pentachloride on the ammonium salt, and the product was reduced by the same process as applied to the meta-derivative. The results, however, were unsatisfactory, the yield of sulphinic acid being extremely poor and the process of isolation difficult. Moreover, the acid obtained, although agreeing in all other properties with that described by Gattermann (*Ber.*, 1899, **32**, 1144), differs from this in the melting point given by that author. Gattermann states that the melting point of *o*-carboxybenzenesulphinic acid is 125°, but this is evidently a misprint, for on preparing the acid by the diazo-process we found that the product was identical with that yielded by the reduction method; both, when heated, assume a yellow colour at about 200°, and do not melt below 270°. A sample was recrystallised from glacial acetic acid, and then analysed. (Found, C = 44·8; H = 3·5. Calc., C = 45·17; H = 3·22 per cent.) Gattermann has shown, from the action of hydroxylamine on this substance, that it is a sulphinic acid, and we have further confirmed this structure by the behaviour with phenetole in concentrated sulphuric acid. In preparing this acid, the diazo-process is to be recommended in preference to the reduction method, on account of the better yields, for 20 grams of anthranilic acid yielded about 18 grams of the sulphinic acid.

Thioxanthone,

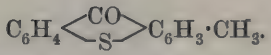


$$C_6H_4<\substack{CO\\S}>C_6H_4.$$

(*a*) *From* o-*Carboxybenzenesulphinic Acid.*—Ten grams of *o*-carboxybenzenesulphinic acid were suspended in an excess of cold concentrated sulphuric acid, and excess of benzene was gradually added to the mixture, which was constantly shaken for about four hours. After the first addition of benzene the mixture assumed a deep blue colour, indicating the presence of a sulphoxide; but this disappeared as the reaction proceeded, giving place to the strongly fluorescent, yellow solution of thioxanthone. At the same time sulphurous acid was evolved. The mixture was then set aside at the atmospheric temperature for a further nine hours, and was subsequently heated for one hour on the water-bath. The solution was poured on powdered ice, and the precipitate which formed was collected, washed with water, thoroughly triturated with 10 per cent. aqueous alkali hydroxide, again collected, and finally washed with water until free from alkali. The dried substance was purified by extraction with chloroform in a Soxhlet apparatus; the extract was evaporated, and the residue was further purified by crystallisation from hot glacial acetic acid. The substance melted at 209°, and all other properties, such as colour, fluorescence, crystalline form, and solubility, agreed with those elsewhere attributed to thioxanthone. When mixed with thioxanthone from other sources, it melted at the same temperature. The yield of thioxanthone obtained by this process was about 60 per cent. of the theoretical, 7 grams being furnished by 10 grams of the sulphinic acid.

(*b*) *From* o-*Thiolbenzoic Acid.*—The preparation of thioxanthone from *o*-thiolbenzoic acid was conducted in a similar manner and under the same conditions as that described in the foregoing paragraph. The reaction proceeds somewhat more energetically, sulphurous acid being continually evolved during the process. Ten grams of *o*-thiolbenzoic acid gave 12·5 grams of thioxanthone, or about 90 per cent. of that required by theory. After purification the substance melted at 209°. (Found, C = 73·3; H = 3·8; S = 15·41. Calc., C = 73·6; H = 3·8; S = 15·1 per cent.) The substance was reduced with phosphorus and hydriodic acid, when thioxanthene was obtained.

Methylthioxanthone,



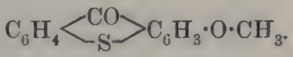
$$C_6H_4\genfrac{<}{>}{0pt}{}{CO}{S}C_6H_3\cdot CH_3.$$

This substance was prepared from *o*-thiolbenzoic acid and toluene in concentrated sulphuric acid, the minor details of the process being the same as those already described. When crystallised from hot acetone, the substance appears to retain some impurity of lower carbon content; it was therefore further purified by distillation, which may be conducted under the ordinary pressure with small quantities without decomposition. *Methylthioxanthone* was obtained in this way as a pale yellow, crystalline solid, which melted at 96—97°. It is very soluble in most organic media, sparingly so in ether, and insoluble in water. It sublimes slowly when heated to about 150°, and is then obtained in very pale yellow needles:

0·1072 gave 0·2900 CO_2 and 0·0424 H_2O. C = 73·8; H = 4·39.

$C_{14}H_{10}OS$ requires C = 74·3; H = 4·43 per cent.

Methoxythioxanthone,



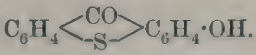
$$C_6H_4\genfrac{<}{>}{0pt}{}{CO}{S}C_6H_3\cdot O\cdot CH_3.$$

The preparation from anisole and *o*-thiolbenzoic acid was conducted in the usual manner. The product was crystallised from chloroform, and was obtained in bright yellow needles, which melted at 129°. It is soluble in most organic media, the solution in glacial acetic acid showing a strong violet fluorescence. The yield was about 80 per cent. of the theoretical:

0·2014 gave 0·5107 CO_2 and 0·0823 H_2O. C = 69·16; H = 4·5.
0·2450 „ 0·2447 $BaSO_4$. S = 13·7.
0·2076 „ 0·1589 AgI. OMe = 12·0.

$C_{14}H_{10}O_2S$ requires C = 69·4; H = 4·1; S = 13·3; OMe = 12·8 per cent.

Hydroxythioxanthone,



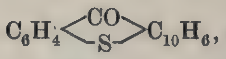
$$C_6H_4\genfrac{<}{>}{0pt}{}{CO}{S}C_6H_4\cdot OH.$$

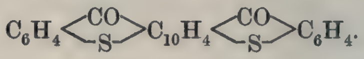
This was prepared from phenol and *o*-thiolbenzoic acid as usual. The precipitate obtained by pouring the acid solution into water was collected, and, after being washed with water, was dissolved in aqueous sodium hydroxide. This solution of the sodium salt was saturated with carbon dioxide, when the phenol was liberated as a yellow, crystalline powder. It was collected, dried, and then extracted with chloroform. The solvent was evaporated, and the residue crystallised from moist acetone. Two different samples of the crystals were analysed:

0·1852 gave 0·4520 CO_2 and 0·0534 H_2O. C = 65·1; H = 3·2.
0·1338 „ 0·3175 CO_2 „ 0·0448 H_2O. C = 64·7; H = 3·7.

$C_{13}H_8O_2S,\frac{1}{2}H_2O$ requires C = 65·27; H = 3·7 per cent.

It will be observed that the content of carbon is somewhat low for the anhydrous compound, but this seems not to be due to impurity, since the samples analysed were from successive fractions of the crystallisation. Hence it may be assumed that the substance contains water of crystallisation, and this behaviour has been observed with some of the polyhydroxyxanthones. However, attempts to remove water by heating to 100° were unsuccessful. *Hydroxythioxanthone* forms bright yellow prisms, which are readily soluble in most organic media and in aqueous sodium hydroxide, giving orange solutions of the sodium salt; it melts at 214—215°.

Naphthathioxanthone,  $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{S}{>}C_{10}H_6$, *and*

Naphthabisthioxanthone,  $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{S}{>}C_{10}H_4{<}\genfrac{}{}{0pt}{}{CO}{S}{>}C_6H_4$.

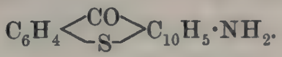
The preparation was conducted in the usual manner. The precipitate obtained on pouring the acid solution into water was apparently colloidal, and it was therefore isolated by removing the mother liquor with a Pukall's filter. The removal of carboxylic acids in the form of sodium salts and the final washing with water was effected by the same means. The yellow mass was then treated with a current of steam to remove excess of naphthalene, and, after being dried, it was repeatedly extracted with much acetone. On cooling the solution, the bisthioxanthone separated almost completely in microscopic prisms; these were recrystallised for analysis:

0·1087 gave 0·2898 CO_2 and 0·0309 H_2O. C = 72·69; H = 3·38.
0·1084 „ 0·2872 CO_2 „ 0·0296 H_2O. C = 72·24; H = 3·03.
$C_{24}H_{12}O_2S_2$ requires C = 72·72; H = 3·03 per cent.

Naphthabisthioxanthone is almost insoluble in cold organic media, and it does not melt below 280°. The acetone mother liquor from the bisthioxanthone was evaporated and allowed to cool, when a further small quantity of that substance separated. The filtrates from this were completely evaporated, and the residue recrystallised from acetone. *Naphthathioxanthone* was thus obtained in yellow prisms, which melt at 186°. It is soluble in sulphuric acid, giving a green fluorescence:

0·1271 gave 0·3643 CO_2 and 0·0364 H_2O. C = 78·2; H = 3·2.
0·276, in 20·0 of naphthalene, gave $\Delta t = -0·380°$. M.W. = 262.
$C_{17}H_{10}OS$ requires C = 77·9; H = 3·8 per cent. M.W. = 255.

β-Aminonaphthathioxanthone,



$C_6H_4<\overset{CO}{\underset{S}{}}>C_{10}H_5\cdot NH_2$.

This was prepared as usual from β-naphthylamine and *o*-thiolbenzoic acid. The product was crystallised from hot chloroform, from which it separated in mustard-yellow prisms:

0·1612 gave 0·4333 CO_2 and 0·0530 H_2O. C = 73·35; H = 3·65.
0·2929 „ 0·2445 $BaSO_4$. S = 11·5.
$C_{17}H_{11}ONS$ requires C = 73·65; H = 3·96; S = 11·55 per cent.

β-Aminonaphthathioxanthone melts at 213°. The pale buff-coloured *platinichloride* is insoluble in cold water. The yield of this derivative was good, 5 grams of the pure product being obtained from 5 grams of *o*-thiolbenzoic acid and excess of β-naphthylamine. A small quantity of the corresponding bisthioxanthone was formed, but it was not more closely examined.

In conclusion we desire to thank the Research Fund Committee of the Society for a grant which has defrayed the cost of these experiments.

THE ORGANIC CHEMISTRY LABORATORY,
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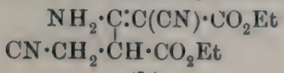
CXVIII.—*The Formation and Reactions of Imino-compounds. Part XIII. The Constitution of Ethyl β-Imino-α-cyanoglutarate and of its Alkyl Derivatives.*

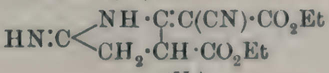
By ARTHUR FRED CAMPBELL and JOCELYN FIELD THORPE.

IN Part X of this series (Trans., 1909, **95**, 1506) an instance was recorded in which the five-membered ring, containing four carbon atoms and one nitrogen atom, was readily formed by the action of sodium ethoxide, or of a sodium compound dissociating in solution, on a γ-amino-nitrile. Thus the open-chain compound represented by formula (I) could not be isolated from the product of the interaction of iodoacetonitrile and the sodium compound of ethyl β-imino-α-cyanoglutarate, the only substance formed being the pyrrole derivative represented by formula (II):



$$\begin{array}{l} NH_2\cdot C{:}C(CN)\cdot CO_2Et \\ CN\cdot CH_2\cdot CH\cdot CO_2Et \end{array}$$

(I.)



$$HN{:}C<\begin{array}{l} NH\cdot C{:}C(CN)\cdot CO_2Et \\ CH_2\cdot CH\cdot CO_2Et \end{array}$$

(II.)

It was also shown that ethyl γ-imino-α-cyanoglutarate reacts entirely as an amino-compound, and that the sodium compound formed from it by the action of alcoholic sodium ethoxide has the constitution:

$$CO_2Et\cdot CHNa\cdot C(NH_2)\colon C(CN)\cdot CO_2Et.$$

In Part I of this series (Trans., 1904, **85**, 1737), in which the alkylation of ethyl β-imino-α-cyanoglutarate was described, it was stated that the introduction of the second methyl group into this molecule led to the displacement of the hydrogen atom attached to the cyanoacetic residue, and not of the remaining hydrogen atom of the methylene group. The proof of this statement was obtained in two ways, first because the dimethyl derivative on complete alkaline hydrolysis gave only methylmalonic acid, and not a mixture of dimethylmalonic and malonic acids, which would have been the case had the two methyl groups been attached to the same carbon atom, thus:

$$CO_2Et\cdot CHMe\cdot C(\colon NH)\cdot CMe(CN)\cdot CO_2Et \longrightarrow CHMe(CO_2H)_2 + CHMe(CO_2H)_2,$$

$$CO_2Et\cdot CMe_2\cdot C(\colon NH)\cdot CH(CN)\cdot CO_2Et \longrightarrow CMe_2(CO_2H)_2 + CH_2(CO_2H)_2,$$

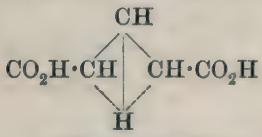
and secondly because the same dimethyl derivative was formed by the condensation of ethyl α-cyanopropionate with its sodium derivative, thus:

$$CO_2Et\cdot CNaMe\cdot CN + H\cdot CMe(CN)\cdot CO_2Et \longrightarrow CO_2Et\cdot CNaMe\cdot C(\colon NH)\cdot CMe(CN)\cdot CO_2Et \longrightarrow CO_2Et\cdot CHMe\cdot C(\colon NH)\cdot CMe(CN)\cdot CO_2Et.$$

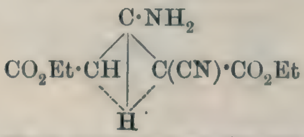
Since that time, however, it has been ascertained that compounds of this type are true amino-compounds which exhibit no chemical evidence of reacting in an imino-form, and hence it follows that before the methyl group can enter the cyanoacetic residue a shifting of the double bond must ensue about the central carbon atom, thus:

$CO_2Et\cdot CHNa\cdot C(NH_2)\colon C(CN)\cdot CO_2Et$	1st sodium compound.
$CO_2Et\cdot CHMe\cdot C(NH_2)\colon C(CN)\cdot CO_2Et$	Monomethyl derivative.
$CO_2Et\cdot CMe\colon C(NH_2)\cdot CNa(CN)\cdot CO_2Et$	2nd sodium compound.
$CO_2Et\cdot CMe\colon C(NH_2)\cdot CMe(CN)\cdot CO_2Et$	Dimethyl derivative.

A change of this kind would suggest the presence of an alternating (mobile) hydrogen atom capable of passing between the α- and α′-carbon atoms similar to that which it was suggested might be present in the molecule of glutaconic acid, and thus account for the identity of the α- and γ- (or α′-) positions:

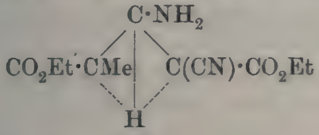


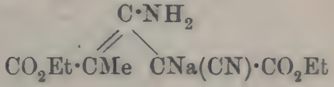
(Glutaconic acid.)



(Ethyl β-imino-α-cyanoglutarate.)

If this view is correct, the methylation of the amino-nitrile would lead to the formation of a monomethyl derivative represented by formula (III), which, on treatment with sodium ethoxide, would yield a sodium compound represented by formula (IV):

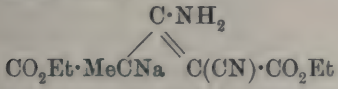

(III.)

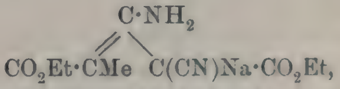

(IV.)

This view depends entirely on the assumption that the compound is a true amino-compound, because, if it can be shown that it possesses an imino-phase, the "wandering" of the double bond can be explained as follows:

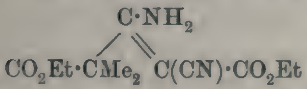
$$CO_2Et\cdot CMeH\cdot C(NH_2){:}C(CN)\cdot CO_2Et \longrightarrow$$
$$CO_2Et\cdot CMeH\cdot C({:}NH)\cdot CH(CN)\cdot CO_2Et$$
$$\downarrow$$
$$CO_2Et\cdot CMe{:}C(NH_2)\cdot CH(CN)\cdot CO_2Et.$$

The experimental evidence on this point has, however, led us to the conclusion that a compound of the above type does not possess an imino-phase, but reacts only in the amino-form (Trans., 1909, **95**, 1508). If this is so, and we adduce some further evidence on this point later, then it might be expected that the swing of the hydrogen atom would lead to the formation of two sodium compounds, thus:

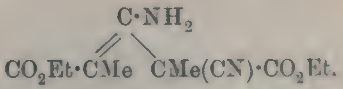




and that on methylation two isomeric dimethyl derivatives would be formed having the constitutions:



and



We have carefully repeated the work previously done, using larger quantities of material, which we have subjected to an exhaustive process of fractional recrystallisation, and have succeeded, not only in isolating the two isomeric dimethyl derivatives represented above, but have been able to obtain one of them (the *aa*-dimethyl derivative) in its stereoisomeric *cis*- and *trans*-forms.

The recently published work by Feist on the alkylglutaconic acids (*Annalen*, 1909, **370**, 41), together with his previous paper on this subject (*Annalen*, 1906, **345**, 77), shows that the explanation advanced by one of us (Trans., 1905, **87**, 1669) to account for the fact that glutaconic acid and several of its derivatives cannot be obtained in *cis*- and *trans*-forms corresponding with maleic and fumaric acid does not apply to the monoalkyl derivatives of glutaconic acid, because β-methylglutaconic acid,

$$CO_2H\cdot CH\colon CMe\cdot CH_2\cdot CO_2H$$

(*Annalen*, 1906, **345**, 77), and α-methylglutaconic acid,

$$CO_2H\cdot CMe\colon CH\cdot CH_2\cdot CO_2H$$

(*Annalen*, 1909, **370**, 61), can be isolated in *cis*- and *trans*-forms.

Still, as we explained some time ago (Proc., 1906, **22**, 146), this does not necessarily show that our suggestion as to the constitution of glutaconic acid is wrong, because it is quite conceivable that the entering of a methyl group may so affect the mobility of the hydrogen atom, owing to steric conditions or otherwise, as to bring about the fixing of the double bond, and hence lead to the conditions which allow the *cis*- and *trans*-forms to exist.

Until it can be shown that glutaconic acid can be isolated in *cis*- and *trans*-modifications, we maintain that our explanation of the constitution of this acid is the one most in accordance with the experimental facts.

Apart, however, from any considerations of this kind, it is certain that whenever the conditions arise in the molecule of the alkylglutaconic acids which, according to our view, causes the certain fixation of the double bond, then the phenomenon of stereoisomerism always occurs, and the *cis*- and *trans*-forms can be isolated without difficulty. This is always the case in derivatives of glutaconic acid when the two α-hydrogen atoms are substituted, thus: $CO_2H\cdot CR_2\cdot CH\colon CH\cdot CO_2H$, and, therefore, in the analogous case of ethyl β-imino-α-cyanoglutarate, should also occur when the corresponding hydrogen atoms are displaced, as is the case in both the **αα**- and **αα′**-dimethyl derivatives, thus:

αα′-Dimethyl derivative, $CO_2Et\cdot CMe\colon C(NH_2)\cdot CMe(CN)\cdot CO_2Et$.

αα-Dimethyl derivative, $CO_2Et\cdot CMe_2\cdot C(NH_2)\colon C(CN)\cdot CO_2Et$.

The great difficulty entailed by separating five different substances by fractional recrystallisation has prevented us up to the present from being able to isolate the two forms of the **αα′**-dimethyl derivative, but, as already mentioned, we have separated the *cis*- and *trans*-forms of the **αα**-dimethyl derivative, which are well-defined crystalline substances, the constitutions of which are clearly shown by the products they yield on hydrolysis.

Before proceeding with the separation of these dimethyl derivatives, we decided, in the first instance, to investigate the monomethyl derivative,

$$CO_2Et\cdot CHMe\cdot C(NH_2)\colon C(CN)\cdot CO_2Et,$$

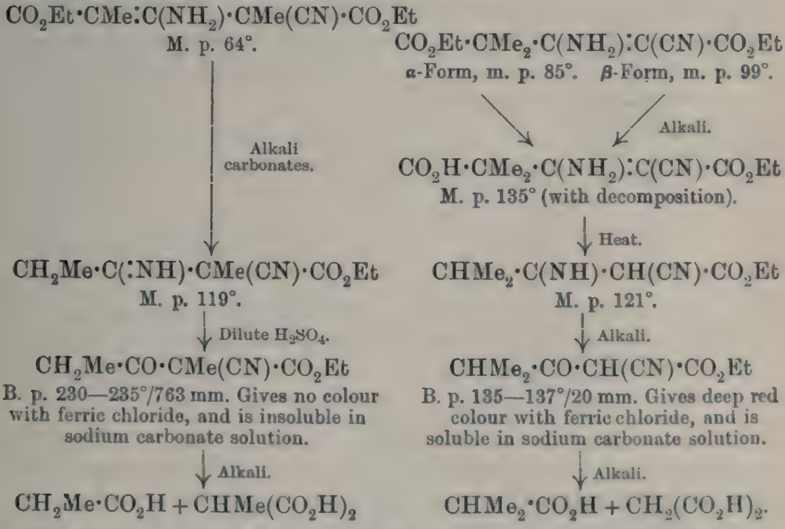
in order to ascertain whether it could be isolated in *cis*- and *trans*-modifications.

With this object in view, we prepared large quantities of this compound, both by the direct methylation of the sodium compound formed in the condensation of ethyl cyanoacetate and its sodium derivative:

$$\mathrm{CO_2Et{\cdot}CHNa{\cdot}CN + H{\cdot}CH(CN){\cdot}CO_2Et \longrightarrow CO_2Et{\cdot}CHNa{\cdot}C(NH_2){:}C(CN){\cdot}CO_2Et}$$
$$\downarrow$$
$$\mathrm{CO_2Et{\cdot}CHMe{\cdot}C(NH_2){:}C(CN){\cdot}CO_2Et}$$

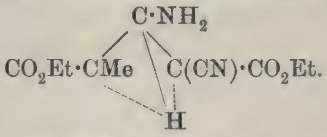
and by the alkylation of pure ethyl β-imino-α-cyanoglutarate by means of sodium ethoxide and methyl iodide. The product in each case was found to be a pure homogeneous compound, which, although subjected to repeated fractional recrystallisation, failed to reveal the presence of any second substance.

The methyl derivative was then further methylated in the usual manner, and from the portion soluble in benzene three substances were isolated by fractional recrystallisation from dilute alcohol, and finally obtained pure. Their behaviour, as indicated in the following table, clearly indicated their structure:

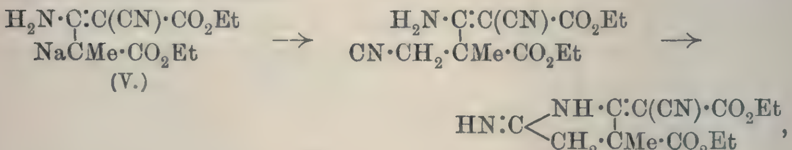

$\mathrm{CO_2Et{\cdot}CMe{:}C(NH_2){\cdot}CMe(CN){\cdot}CO_2Et}$
M. p. 64°.
$\mathrm{CO_2Et{\cdot}CMe_2{\cdot}C(NH_2){:}C(CN){\cdot}CO_2Et}$
α-Form, m. p. 85°. β-Form, m. p. 99°.
$\mathrm{CO_2H{\cdot}CMe_2{\cdot}C(NH_2){:}C(CN){\cdot}CO_2Et}$
M. p. 135° (with decomposition).
$\mathrm{CH_2Me{\cdot}C({:}NH){\cdot}CMe(CN){\cdot}CO_2Et}$
M. p. 119°.
$\mathrm{CHMe_2{\cdot}C(NH){\cdot}CH(CN){\cdot}CO_2Et}$
M. p. 121°.
$\mathrm{CH_2Me{\cdot}CO{\cdot}CMe(CN){\cdot}CO_2Et}$
B. p. 230—235°/763 mm. Gives no colour with ferric chloride, and is insoluble in sodium carbonate solution.
$\mathrm{CHMe_2{\cdot}CO{\cdot}CH(CN){\cdot}CO_2Et}$
B. p. 135—137°/20 mm. Gives deep red colour with ferric chloride, and is soluble in sodium carbonate solution.
$\mathrm{CH_2Me{\cdot}CO_2H + CHMe(CO_2H)_2}$
$\mathrm{CHMe_2{\cdot}CO_2H + CH_2(CO_2H)_2}$.

The terms α- and β-forms are used because it was not found possible to decide between the *cis*- and *trans*-modifications.

It is evident therefore that the second methyl group unites with both the α- and α′-carbon atoms of ethyl β-imino-α-cyanoglutarate, although we find that the amount of the αα-dimethyl derivative formed is very much less than that of the αα′-dimethyl derivative. These facts are in accordance with the assumption that the hydrogen atom of ethyl β-imino-α′-cyano-α-methylglutarate alternates between the *α*- and *α′*-carbon atoms as in glutaconic acid, but that the period of time during which the hydrogen atom is attached to the *α′*-carbon atom is greater than that during which it is attached to the *α*-carbon atom. This could be represented graphically thus:



So far as could be judged from the quantity of the *αα*-dimethyl derivative formed in the above methylation, the amount was not more than 15 per cent. of the total product, and it is evident therefore that the phase during which the hydrogen atom swings towards the *α*-carbon atom is very short. In order therefore to settle this point with greater certainty, we decided to treat the sodium compound of ethyl *β*-imino-*α′*-cyano-*α*-methylglutarate with iodoacetonitrile, because, whether the sodium atom acted on the *α*- or *α′*-carbon atom, a pyrrole derivative would be formed, which could easily be isolated and identified. The formation of pyrrole derivatives in this manner has been already described (Trans., 1909, **95**, 1506), and, therefore, if, in the above condensation, the sodium acted on the *α*-carbon atom (V) a pyrrole derivative (VI) would be formed, thus:



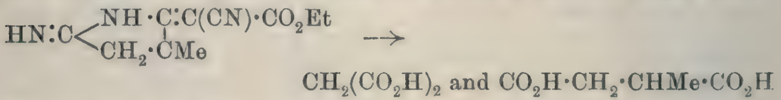
$$\begin{array}{l} H_2N\cdot C{:}C(CN)\cdot CO_2Et \\ \quad NaCMe\cdot CO_2Et \end{array} \longrightarrow \begin{array}{l} H_2N\cdot C{:}C(CN)\cdot CO_2Et \\ CN\cdot CH_2\cdot CMe\cdot CO_2Et \end{array} \longrightarrow$$

(V.)

$$HN{:}C{<}\begin{array}{l} NH\cdot C{:}C(CN)\cdot CO_2Et \\ CH_2\cdot CMe\cdot CO_2Et \end{array},$$

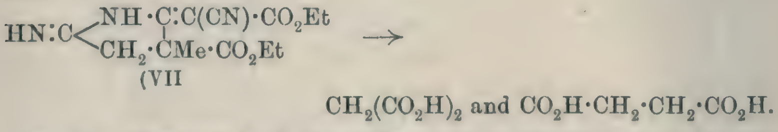
(VI.)

and this compound would undergo disruption with strong alkalis, yielding a mixture of methylsuccinic acid and malonic acids, thus:



$$HN{:}C{<}\begin{array}{l} NH\cdot C{:}C(CN)\cdot CO_2Et \\ CH_2\cdot CMe \end{array} \longrightarrow CH_2(CO_2H)_2 \text{ and } CO_2H\cdot CH_2\cdot CHMe\cdot CO_2H$$

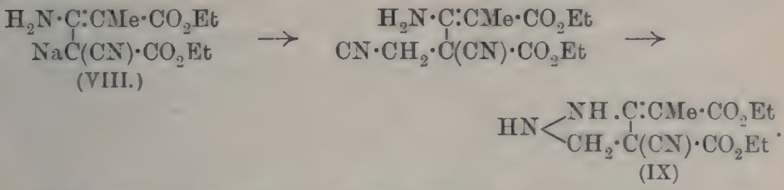
in the same manner as ethyl 2-imino-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate (VII) (Trans., 1909, **95**, 1513), which yields under these conditions a mixture of succinic and malonic acids:



$$HN{:}C{<}\begin{array}{l} NH\cdot C{:}C(CN)\cdot CO_2Et \\ CH_2\cdot CMe\cdot CO_2Et \end{array} \longrightarrow CH_2(CO_2H)_2 \text{ and } CO_2H\cdot CH_2\cdot CH_2\cdot CO_2H.$$

(VII

On the other hand, if the sodium atom attached itself to the cyanoacetic residue as in formula (VIII), the action of iodoacetonitrile would produce a pyrrole derivative corresponding with formula (IX):



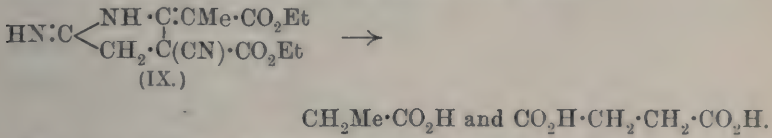
$$\begin{array}{l} H_2N\cdot C{:}CMe\cdot CO_2Et \\ \quad NaC(CN)\cdot CO_2Et \end{array} \longrightarrow \begin{array}{l} H_2N\cdot C{:}CMe\cdot CO_2Et \\ CN\cdot CH_2\cdot C(CN)\cdot CO_2Et \end{array} \longrightarrow$$

(VIII.)

$$HN{<}\begin{array}{l} NH\,.\,C{:}CMe\cdot CO_2Et \\ CH_2\cdot C(CN)\cdot CO_2Et \end{array}.$$

(IX)

It is difficult to predict the manner in which this pyrrole derivative would undergo disruption on alkaline hydrolysis, but if it behaved in the same manner as ethyl 2-imino-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate, it would yield succinic acid (or ethanetricarboxylic acid) and propionic acid, thus:

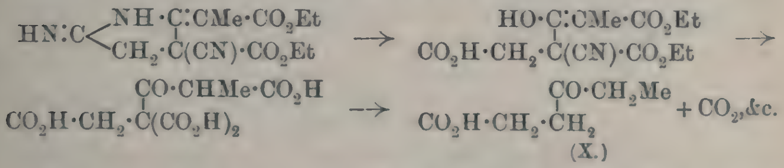


$$HN{:}C{<}\begin{array}{l} NH\cdot C{:}CMe\cdot CO_2Et \\ CH_2\cdot C(CN)\cdot CO_2Et \end{array} \longrightarrow$$

(IX.)

$$CH_2Me\cdot CO_2H \text{ and } CO_2H\cdot CH_2\cdot CH_2\cdot CO_2H.$$

But as a matter of fact the pyrrole derivative which is formed by the action of iodoacetonitrile on the sodium compound of ethyl β-imino-α′-cyano-α-methylglutarate undergoes disruption in another manner, which, however, clearly shows that it possesses a constitution represented by formula (IX), for the product consists of homolævulic acid (X), carbon dioxide, and ammonia. The disruption has therefore taken place in the following way:



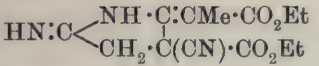
$$HN{:}C{<}\begin{array}{l} NH\cdot C{:}CMe\cdot CO_2Et \\ CH_2\cdot C(CN)\cdot CO_2Et \end{array} \longrightarrow \begin{array}{r} HO\cdot C{:}CMe\cdot CO_2Et \\ CO_2H\cdot CH_2\cdot C(CN)\cdot CO_2Et \end{array} \longrightarrow$$

$$\begin{array}{r} CO\cdot CHMe\cdot CO_2H \\ CO_2H\cdot CH_2\cdot C(CO_2H)_2 \end{array} \longrightarrow \begin{array}{r} CO\cdot CH_2Me \\ CO_2H\cdot CH_2\cdot CH_2 \end{array} + CO_2, \&c.$$

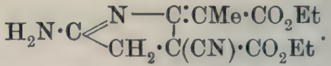
(X.)

The formation of the compound of formula (IX), which we have called *ethyl 2-imino-4-cyano-4-carbethoxytetrahydropyrrolidene-5-α-propionate*, is therefore not only another instance of the formation of the pyrrole ring from a γ-amino-nitrile, but its formation also supplies clear proof of the predominant position of the second sodium atom entering the molecule of ethyl β-imino-α-cyanoglutarate. We were quite unable to detect the presence of the pyrrole derivative corresponding with formula (VI), and, in the condensation, the whole of the amino-ester not condensed to form the above-mentioned pyrrole derivative of formula (IX) was recovered unchanged.

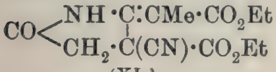
Ethyl 2-imino-4-cyano-4-carbethoxytetrahydropyrrolidene-5-α-propionate is a tautomeric amino-imino- (ketimino-enamic) compound reacting in the two forms:


$$\mathrm{HN{:}C}<\begin{matrix}\mathrm{NH\cdot C{:}CMe\cdot CO_2Et}\\ \mathrm{CH_2\cdot C(CN)\cdot CO_2Et}\end{matrix}$$

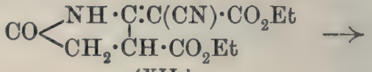
and


$$\mathrm{H_2N\cdot C}<\begin{matrix}\mathrm{N{-}C{:}CMe\cdot CO_2Et}\\ \mathrm{CH_2\cdot C(CN)\cdot CO_2Et}\end{matrix}.$$

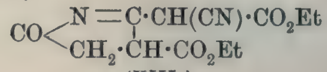
It melts at 216°, and is converted either by hydrochloric acid or by nitrous acid into *ethyl 4-cyano-2-keto-4-carbethoxytetrahydropyrrolidene-5-α-propionate* (XI). This ketone is instantly soluble in sodium carbonate solution, and is therefore the pyrrole form as represented above. This form is, moreover, stable, and does not appear to pass into the *iso*pyrrole form corresponding with the transformation of ethyl 2-keto-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate (XII) into ethyl 2-keto-4-carbethoxydihydro*iso*pyrrolyl-5-cyanoacetate (XIII):


$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot C{:}CMe\cdot CO_2Et}\\ \mathrm{CH_2\cdot C(CN)\cdot CO_2Et}\end{matrix}$$

(XI.)


$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot C{:}C(CN)\cdot CO_2Et}\\ \mathrm{CH_2\cdot CH\cdot CO_2Et}\end{matrix} \longrightarrow$$

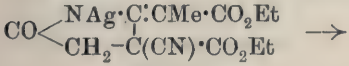
(XII.)


$$\mathrm{CO}<\begin{matrix}\mathrm{N{=}C\cdot CH(CN)\cdot CO_2Et}\\ \mathrm{CH_2\cdot CH\cdot CO_2Et}\end{matrix}$$

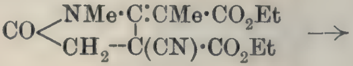
(XIII.)

(compare Trans., 1909, **95**, 1512).

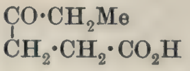
It forms salts with alkalis, having the metal attached to the nitrogen atom; when the silver salt (XIV) is treated with methyl iodide, an N-*methyl* derivative (XV) is formed, the constitution of which is proved by the formation of homolævulic acid, methylamine, and ammonia from it on alkaline hydrolysis:


$$\mathrm{CO}<\begin{matrix}\mathrm{NAg\cdot C{:}CMe\cdot CO_2Et}\\ \mathrm{CH_2{-}C(CN)\cdot CO_2Et}\end{matrix} \longrightarrow$$

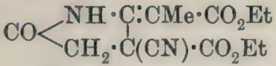
(XIV.)


$$\mathrm{CO}<\begin{matrix}\mathrm{NMe\cdot C{:}CMe\cdot CO_2Et}\\ \mathrm{CH_2{-}C(CN)\cdot CO_2Et}\end{matrix} \longrightarrow$$

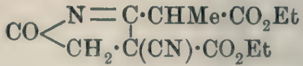
(XV.)


$$\begin{matrix}\mathrm{CO\cdot CH_2Me}\\ \mathrm{CH_2\cdot CH_2\cdot CO_2H}\end{matrix} + \mathrm{NH_2Me}, \text{\&c.}$$

It is evident therefore that the desmotropism of the pyrrole and *iso*pyrrole forms of these compounds is determined by the cyanoacetic residue outside the pyrrole ring, and that it ceases when a less negative group is in this position. Whether or not the two forms:


$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot C{:}CMe\cdot CO_2Et}\\ \mathrm{CH_2\cdot C(CN)\cdot CO_2Et}\end{matrix}$$

and


$$\mathrm{CO}<\begin{matrix}\mathrm{N{=}C\cdot CHMe\cdot CO_2Et}\\ \mathrm{CH_2\cdot C(CN)\cdot CO_2Et}\end{matrix}$$

are tautomeric, we have at present no means of ascertaining, although it is highly probable that they are so.

Our conclusions are therefore as follows.

(1) That ethyl β-imino-α-cyanoglutarate is constituted in an analogous manner to glutaconic acid, that is to say, there is tautomerism between the α- and α′-carbon atoms.

(2) That the first hydrogen displaced by sodium on treating this substance with sodium ethoxide is not the mobile hydrogen atom producing tautomerism, but the remaining hydrogen atom attached to the α-carbon atom.

(3) That when this hydrogen atom is replaced the tautomeric nature of the compound becomes evident, because the next sodium atom unites with either the α- or α'-carbon atom.

(4) That so long as the mobile hydrogen atom remains, stereoisomeric forms cannot be isolated, but so soon as the double bond is fixed by the entrance of two methyl groups, the compound can exist in *cis*- and *trans*-forms.

EXPERIMENTAL.

Ethyl β-Imino-α'-cyano-α-methylglutarate, $CO_2Et\cdot CHMe\cdot C(NH_2){:}C(CN)\cdot CO_2Et$.

The preparation of this substance in large quantities was effected in two different ways in order to see whether by varying the method of production any difference in the composition of the product could be detected.

(1) *From the sodium compound formed in the condensation of ethyl cyanoacetate with its sodium derivative, by treatment with methyl iodide.*—This is by far the best method for obtaining large quantities of the pure methyl derivative, and as the process was used for the production of the methyl derivative employed in this research and differed from that previously given (Trans., 1904, **85**, 1747), it is advisable to give the full experimental details. 11·5 Grams of sodium were dissolved in 150 grams of alcohol, the solution was mixed with 113 grams of ethyl cyanoacetate, and then heated on the water-bath for two hours. At the end of this time the clear, brownish-coloured solution was cooled and mixed with 75 grams of methyl iodide, the solution being heated on the water-bath for a further two hours. Water was then added, and the product distilled in a current of steam until the distillate became free from oil. The residue in the flask, which solidified on cooling, was then collected by filtration.

(2) *From Ethyl β-Imino-α-cyanoglutarate by treatment with sodium ethoxide and methyl iodide.*—The process adopted in this case was essentially the same as above, pure ethyl β-imino-α-cyanoglutarate, prepared as already described (Trans., 1909, **95**, 1518), being treated in alcoholic solution with an equivalent amount of sodium dissolved in alcohol, and then with a slight excess of methyl iodide, the reaction being completed by heating on the water-bath for two hours. The product was purified and isolated by steam distillation in the manner described above.

The solid product prepared by each of these methods was then separately subjected to a process of fractional recrystallisation from dilute alcohol. The melting point of each fraction was 63—64°, the melting point previously found for ethyl β-imino-α′-cyano-α-methylglutarate, and allowing for a small quantity of oily product which could not be obtained crystalline, it can be stated with certainty that no other compound is formed in these reactions.

As the method of fractional recrystallisation from dilute alcohol in this case was the same as that adopted with the dimethyl derivatives described below, the opportunity may be taken of briefly describing it. In every case the solid substance was dissolved in warm alcohol, and, after the solution had been cooled, sufficient water was added until it became cloudy, when a drop of alcohol again produced a clear solution, which was allowed to remain. In the course of a few hours, crystals had separated, which were collected. Water was then added to the mother liquor until it was again cloudy, when alcohol was added until clear, and a fresh crop of crystals obtained by keeping the solution for some time. This process was repeated until the mother liquor ceased to give a precipitate of oil on the addition of water. In this way several fractions were obtained, which were each subjected to the same process, the fractions being combined and recrystallised together so soon as they showed the same melting point.

The Methylation of Ethyl β-Imino-α′-cyano-α-methylglutarate.

As it was found that by the complete methylation of ethyl β-imino-α′-cyano-α-methylglutarate under the condition employed only one methyl group could be introduced, the methylation of this compound to form the dimethyl derivative was effected by means of excess of sodium ethoxide and methyl iodide, the operation being carried out twice. This was found to be necessary, because, when the compound was methylated once only, some unchanged monomethyl derivative was always found in the product.

(1) *Ethyl β-Imino-α-cyanovalerate,*
$CH_3\cdot CH_2\cdot C(:NH)\cdot CH(CN)\cdot CO_2Et$.

This substance is always formed in the above methylation, owing to the elimination of a carbethoxy-group from ethyl β-imino-α′-cyano-α-methylglutarate by the action of sodium ethoxide. It appeared to be impossible to prevent this action even by keeping the temperature very low. The method adopted to effect methylation was as follows. Twenty-four grams of ethyl β-imino-α′-cyano-α-methylglutarate were mixed with a solution of 3 grams of sodium dissolved in 50 grams of alcohol, and 16 grams of methyl iodide added. After the solution had been heated on the water-bath until a test portion showed a neutral reaction on dilution, water was added, and the oil extracted with ether. The residue left on evaporating the ether was then again treated with 3 grams of sodium dissolved in alcohol and 16 grams of methyl iodide in the same manner as above, when the ultimate product, which became solid, was spread on a porous plate until free from oil.

The solid residue was then rubbed with cold benzene, in which the greater portion dissolved, leaving a crystalline substance, which, after being twice recrystallised from benzene, yielded fern-shaped crystals, melting at 121°:

0·2021 gave 0·4254 CO_2 and 0·1295 H_2O. C=57·41; H=7·12.
$C_8H_{12}O_2N_2$ requires C=57·1; H=7·1 per cent.

The analytical data and the formation of ethyl α-cyano-β-ketovalerate, $CH_3\cdot CH_2\cdot CO\cdot CH(CN)\cdot CO_2Et$ (Found, C=56·88; H=6·45. Calc., C=56·8; H=6·5 per cent.), from this substance, on treatment with dilute potassium hydroxide, showed it to be ethyl β-imino-α-cyanovalerate.

It may be mentioned here that by far the best method for transforming an imino-compound of the type

$$R\cdot C(:NH)\cdot CH(CN)\cdot CO_2Et$$

into the corresponding ketone is by warming it with aqueous potassium hydroxide solution until all has dissolved, and then acidifying the clear solution in order to precipitate the ketone. These compounds are tautomeric ketimino-enamic derivatives having a longer enamic than ketimino-phase. They are consequently only slowly hydrolysed by acids, whereas with alkalis they are rapidly transformed into the alkali salt, $R\cdot C(OK):C(CN)\cdot CO_2Et$, which is very stable towards boiling alkalis.

(2) *The α- and β-forms of Ethyl β-Imino-α′-cyano-αα-dimethylglutarate*, $CO_2Et\cdot CMe_2\cdot C(NH_2):C(CN)\cdot CO_2Et$.

The benzene solution obtained in the above separation was evaporated to dryness, and the residue again triturated with cold benzene, when a further small quantity of the substance melting at 121° was obtained. The solid residue, after again evaporating the benzene, was then fractionally recrystallised from dilute alcohol in the manner already described. The first fractions indicated the presence of some substance much less soluble in the solvent than the other constituents of the mixtures. This was therefore collected, and finally obtained pure by recrystallisation from absolute alcohol, from which solvent it separated in long, silky needles, melting at 99°:

0·1937 gave 0·4027 CO_2 and 0·1254 H_2O. C=56·70; H=7·20.
$C_{12}H_{18}O_4N_2$ requires C=56·70; H=7·1 per cent.

The above *α*-form of ethyl *β*-imino-*α′*-cyano-*αα*-dimethylglutarate is so much less soluble in dilute alcohol than the other substances present in the mixture that its separation is a comparatively simple matter.

The residues from which the substance melting at 99° had been, so far as possible, separated were then subjected to a further process of fractional recrystallisation, and ultimately two more compounds were isolated in a pure condition. The first of these, which was found to be present in large quantities, separated from dilute methyl alcohol in small prisms, melting at 64°:

0·1790 gave 0·3740 CO_2 and 0·1167 H_2O. C=56·42; H=7·25.
$C_{12}H_{18}O_4N_2$ requires C=56·70; H=7·1 per cent.

Since this compound showed all the reactions of ethyl *β*-imino-*α′*-cyano-*αα′*-dimethylglutarate,

$$CO_2Et\cdot CMe{:}C(NH_2)\cdot CMe(CN)\cdot CO_2Et,$$

already described (Trans., 1904, **85**, 1751), its constitution is evidently represented by this formula. The second substance, which was present in small amount, was obtained from the mother liquors after the substance melting at 64° had been, so far as possible, separated. It was ultimately obtained from dilute methyl alcohol in large, rectangular prisms, melting at 85°:

0·1862 gave 0·3925 CO_2 and 0·1209 H_2O. C=57·51; H=7·22.
$C_{12}H_{18}O_4N_2$ requires C=56·70; H=7·1 per cent.

The reactions of this compound, given below, showed that it had the same structural formula as that of the compound melting at 99°. It was therefore recrystallised several times in order to ascertain whether it was an impure form of this compound. Recrystallisation, however, failed to alter the melting point, and this fact, together with the well-defined crystalline form, which is quite different from that of the compound melting at 99°, showed conclusively that it was a homogeneous substance stereoisomeric with the compound of higher melting point.

The mother liquors yielded further crystalline crops on further dilution, but these possessed indefinite melting points, and by repeated fractional recrystallisation yielded further small quantities of the compounds already described. The ultimate fractions separated as oils, which could not be induced to solidify, and it was not found possible to isolate any crystalline substance from them.

The Products of Hydrolysis of the α- and β-forms of Ethyl β-Imino-α′-cyano-αα-dimethylglutarate.

(1) *Ethyl Hydrogen β-Imino-α′-cyano-αα-dimethylglutarate,* $CO_2H{\cdot}CMe_2{\cdot}C(NH_2){:}C(CN){\cdot}CO_2Et$.

Both the α- and β-forms of ethyl β-imino-α′-cyano-αα-dimethylglutarate yield this hydrogen salt on treatment with potassium hydroxide solution, the conditions found most suitable being as follows. Five grams of the imino-compound were added to a solution of one and a-half times the calculated quantity of potassium hydroxide dissolved in methyl alcohol, and the solution, which became warm, allowed to remain until a test portion gave a clear solution on the addition of water, when the excess of methyl alcohol was evaporated so far as possible under diminished pressure, and dilute hydrochloric acid added to the residue until it gave an acid reaction. The oil, which was precipitated on the addition of the acid, solidified on scratching, and when recrystallised from dilute alcohol yielded small prisms melting at 135° with vigorous evolution of carbon dioxide:

0·1910 gave 0·3712 CO_2 and 0·1083 H_2O. C = 53·00; H = 6·30.
$C_{10}H_{14}O_4N_2$ requires C = 53·1; H = 6·2 per cent.

The hydrogen salt can also be recrystallised from water, but care must be taken not to boil the solution, otherwise some carbon dioxide is evolved.

(2) *Ethyl β-Imino-α-cyano*iso*butylacetate,* $C_3H_7{\cdot}C({:}NH){\cdot}CH(CN){\cdot}CO_2Et$.

This substance is formed by heating the hydrogen ethyl salt described above at 150° until the evolution of carbon dioxide has ceased. For this purpose the salt was placed in a test-tube and heated in a bath of sulphuric acid at the requisite temperature, and as soon as the evolution of gas had ceased, it was cooled, and the solid which then formed was purified by spreading on a porous plate. When recrystallised from dilute alcohol, it formed glistening plates, melting at 121°:

0·1873 gave 0·4063 CO_2 and 0·1315 H_2O. C = 59·16; H = 7·80.
$C_9H_{14}O_2N_2$ requires C = 59·3; H = 7·7 per cent.

(3) *Ethyl Cyano*iso*butyrylacetate,* $C_3H_7{\cdot}CO{\cdot}CH(CN){\cdot}CO_2Et$.

In order to prepare this substance from the above imino-compound, it is necessary to warm it gently with an aqueous solution containing slightly more than the requisite quantity of potassium hydroxide to form the potassium salt,

$$C_3H_7\cdot C(OK)\colon C(CN)\cdot CO_2Et.$$

The complete transformation of the imino-compound into the potassium salt is effected when the whole of the imino-compound has passed into solution, but care must be taken to keep the temperature as low as possible. When the clear alkaline solution is acidified, an oil is precipitated, which, when extracted by ether, yields a clear, mobile liquid boiling, on distillation, at 135—137°/20 mm.:

0·2117 gave 0·4565 CO_2 and 0·1375 H_2O. C = 58·80; H = 7·21.

$C_9H_{13}O_3N$ requires C = 59·0; H = 7·1 per cent.

The ketone dissolves in aqueous sodium carbonate with effervescence, and gives in alcoholic solution a deep red colour with ferric chloride.

The *silver* salt, $C_9H_{12}O_3NAg$, is precipitated as a white, microcrystalline powder on adding the calculated quantity of silver nitrate solution to a neutral solution of the ammonium salt:

0·2512 gave 0·0934 Ag. Ag = 37·17.

$C_9H_{12}O_3NAg$ requires Ag = 37·24 per cent.

(4) iso*Butyric Acid and Malonic Acid.*—These acids form the ultimate products of the hydrolysis of ethyl cyano*iso*butyrylacetate, and can be isolated in the following way. The ketone is dissolved in excess of aqueous potassium hydroxide, and the solution boiled until ammonia ceases to be evolved, when it is acidified with dilute sulphuric acid and distilled in a current of steam until the distillate is no longer acid. The steam distillate is then rendered alkaline with ammonia, and evaporated on the water-bath to a small bulk. Silver nitrate solution is then added, and the precipitated silver salt recrystallised from hot water. (Found, Ag = 55·21. Calc., Ag = 55·38 per cent.) The acid was characterised as *iso*butyric acid by the formation of the calcium salt.

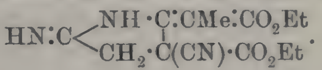
The residue from the steam distillation was then rendered alkaline and evaporated to dryness, the residue being acidified with hydrochloric acid and again evaporated. On extracting the solid residue in a Soxhlet apparatus with ether, a solid residue was obtained, which, when purified, melted at 132°, and was proved to be malonic acid. (Found, C = 34·42; H = 3·8. Calc., C = 34·6; H = 3·8 per cent.)

When ethyl β-imino-α'-cyano-$\alpha\alpha$-dimethylglutarate in either its α- or β-form is boiled with excess of potassium hydroxide until all ammonia has been evolved, the product is found to consist of *iso*butyric acid, dimethylmalonic acid, and malonic acid. The first-named can be isolated by distilling the acidified product of hydrolysis in a current of steam in the manner already described, and the two last, which are extracted by ether from the evaporated residue, can be separated by taking advantage of the fact that dimethylmalonic acid is quite insoluble in cold concentrated hydrochloric acid, whereas malonic acid readily dissolves.

The above experiments were carried out with both the α- and β-forms of ethyl β-imino-α′-cyano-αα-dimethylglutarate, and there can therefore be no doubt as to these two compounds being stereoisomeric. The conditions under which one form is converted into the other could not be determined.

The Formation of Pyrrole Derivatives from Ethyl β-Imino-α′-cyano-α-methylglutarate.

Ethyl 2-Imino-4-cyano-4-carbethoxytetrahydropyrrolidene-5-α-propionate,



$$HN{:}C<\begin{matrix}NH\cdot C{:}CMe{:}CO_2Et\\ \vert \\ CH_2\cdot C(CN)\cdot CO_2Et\end{matrix}.$$

This compound is formed by the action of iodoacetonitrile on the sodium compound of ethyl β-imino-α′-cyano-α-methylglutarate under the following conditions. 2·3 Grams of sodium are dissolved in 50 grams of alcohol, and the solution is mixed with 24 grams of ethyl β-imino-α′-cyano-α-methylglutarate dissolved in as little alcohol as possible. 16·7 Grams of iodoacetonitrile are then added to the cooled solution, and the mixture is heated on the water-bath for ten minutes. After this time the clear solution is poured into water, and the solution extracted by ether, when a crystalline substance remains undissolved and can be isolated by filtration. The ethereal solution deposits more of the substance after some time. The pyrrole derivative obtained in this way crystallises from alcohol in yellow plates, melting at 216°:

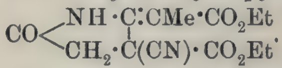
0·1810 gave 0·3715 CO_2 and 0·1070 H_2O. $C=56·02$; $H=6·3$.

$C_{13}H_{17}O_4N_3$ requires $C=55·9$; $H=6·1$ per cent.

The yield of the pyrrole derivatives is very small, being only about 10 per cent. of the theoretical amount, the remainder of the ethyl β-imino-α′-cyano-α-methylglutarate used in the experiment being recovered unchanged on evaporating the ethereal solution after all pyrrole derivative has crystallised out. It is evident, therefore, that under the experimental conditions employed, the major portion of the sodium compound of ethyl β-imino-α′-cyano-α-methylglutarate dissociates in the alcoholic solution, and reacts with iodoacetonitrile as sodium ethoxide. No trace of any other pyrrole derivative could be isolated.

The compound melting at 216° is insoluble in cold aqueous sodium carbonate, but slowly passes into solution on boiling, ammonia being evolved. If the solution is acidified after all ammonia has been given off, the ketone, melting at 128° (see below), is precipitated. It dissolves in cold aqueous potassium hydroxide, forming a solution from which acetic acid precipitates it unchanged. It also dissolves in concentrated hydrochloric acid, forming a clear solution, from which the imino-compound is precipitated by the addition of much water. The compound may be recrystallised from water.

Ethyl 4-*Cyano*-2-*keto*-4-*carbethoxytetrahydropyrrolidene*-5-*α*-*propionate*,



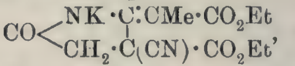
$$CO<\begin{matrix}NH\cdot \overset{}{C}{:}CMe\cdot CO_2Et\\ CH_2\cdot C(CN)\cdot CO_2Et\end{matrix}.$$

When a solution of the imino-compound, melting at 216°, in concentrated hydrochloric acid is poured into an equal volume of boiling water a clear solution is obtained, from which, after the lapse of a few seconds, an oil suddenly separates. This oil solidifies when the solution is cooled and scratched, and the solid then obtained separates from dilute alcohol in small, colourless needles, melting at 128°:

0·1825 gave 0·3721 CO_2 and 0·0972 H_2O. C = 55·81; H = 5·81.

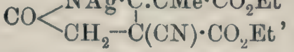
$C_{13}H_{16}O_5N_2$ requires C = 55·7; H = 5·7 per cent.

The ketone gives no colour with ferric chloride, and is soluble in aqueous sodium carbonate, yielding a clear solution, from which acids precipitate it unchanged. There is therefore no tendency for this substance to exhibit desmotropism.

The *potassium* salt,  $CO<\begin{matrix}NK\cdot C{:}CMe\cdot CO_2Et\\ CH_2\cdot C(CN)\cdot CO_2Et\end{matrix}$, is precipitated as an oil when a solution of the ketone in dilute aqueous potassium hydroxide is mixed with excess of the reagent. The oil solidifies on keeping, and can be purified by recrystallisation from a small quantity of ethyl alcohol, from which it separates in small, colourless prisms. It is readily soluble in both ethyl and methyl alcohol:

0·2328 gave 0·0630 K_2SO_4. K = 12·13.

$C_{13}H_{15}O_5N_2K$ requires K = 12·3 per cent.

The *silver* salt,  $CO<\begin{matrix}NAg\cdot C{:}CMe\cdot CO_2Et\\ CH_2-C(CN)\cdot CO_2Et\end{matrix}$, is formed as a gelatinous precipitate when the calculated quantity of silver nitrate solution is added to a solution of the potassium salt in water. It can be dried at 80° without undergoing change, and is then obtained as an amorphous powder, which is characterised by being instantly soluble in dry benzene:

0·2871 gave 0·0798 Ag. Ag = 27·79.

$C_{13}H_{15}O_5N_2Ag$ requires Ag = 27·9 per cent.

Hydrolysis of the Ketone to Homolaevulic Acid.

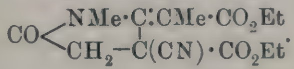
The hydrolysis of ethyl 4-cyano-2-keto-4-carbethoxytetrahydropyrrolidene-5-α-propionate to homolævulic acid is effected in the following manner. Five grams of the ketone are dissolved in excess of aqueous potassium hydroxide, and the solution is boiled until all ammonia has been evolved, when the solution is rendered strongly acid by means of hydrochloric acid, and the acidified solution again boiled until all carbon dioxide has been eliminated. It is then extracted with ether and the ethereal solution evaporated, when a syrup is obtained which distils at 183°/20 mm. as a viscid oil, and solidifies when cooled in a mixture of ice and salt. The solid melts at 32° (compare Zanetti, *Gazzetta*, 1891, **21**, ii, 169; Hillert, *Annalen*, 1892, **268**, 69). (Found, C = 55·27; H = 7·80. Calc., C = 55·4; H = 7·7 per cent.)

The *semicarbazone* separates as a crystalline precipitate when a solution of semicarbazide hydrochloride dissolved in sodium acetate solution is added to an aqueous solution of the ketonic acid. It crystallises from alcohol, in which it is only sparingly soluble, in small prisms, melting and decomposing at 176°:

0·1803 gave 0·2959 CO_2 and 0·1116 H_2O. C = 44·7; H = 6·8.

$C_7H_{13}O_3N_3$ requires C = 44·9; H = 6·9 per cent.

Ethyl 4-*Cyano*-2-*keto*-4-*carbethoxy*-1-*methyltetrahydropyrrolidene*-5-α-*propionate*,



$$CO<\begin{matrix}NMe\cdot \overset{}{C}{:}CMe\cdot CO_2Et\\ \quad | \\ CH_2-C(CN)\cdot CO_2Et\end{matrix}.$$

The above *N*-methyl derivative is best prepared by the action of methyl iodide on the silver salt of the ketone in dry benzene solution. Five grams of the ketone melting at 128° are converted into the silver salt in the manner described on page 1314, and a solution of the dried salt in dry benzene is mixed with excess of methyl iodide. The reaction starts at the ordinary temperature, silver iodide separating as soon as methyl iodide is added, and is completed by warming for a short time on the water-bath. The benzene solution, after being freed from silver iodide by filtration, is then evaporated to dryness, and the oil which remains is allowed to crystallise. It was purified by recrystallisation from dilute methyl alcohol, from which solvent it separated in small plates, melting at 75°:

0·1912 gave 0·3998 CO_2 and 0·1062 H_2O. C = 57·02; H = 6·17.

$C_{14}H_{18}O_5N_2$ requires C = 57·1; H = 6·1 per cent.

Hydrolysis of the N-*Methyl Derivative to Homolaevulic Acid and Methylamine.*

This hydrolysis was effected by the action of aqueous potassium hydroxide in the following manner. Three grams of the *N*-methyl derivative were added to a solution containing one and a-half times the quantity of potassium hydroxide necessary for complete hydrolysis, and the mixture was boiled under conditions which allowed the methylamine formed to be collected (compare Trans., 1909, **95**, 1530). The hydrolysis proceeded rapidly, and was finished at the end of half an hour. The residue in the flask was then acidified, boiled until free from carbon dioxide, and extracted with ether. The ethereal extract, on being evaporated, yielded a syrup, which solidified on cooling, and melted at 32°. It yielded a semicarbazone, melting and decomposing at 176°, and was therefore homolævulic acid. (Found, $C=44{\cdot}77$; $H=6{\cdot}78$. Calc., $C=44{\cdot}9$; $H=6{\cdot}9$ per cent.)

The hydrochloric acid solution into which the volatile products of the hydrolysis had been led was then evaporated to a small bulk, and the solution, after being mixed with excess of platinic chloride solution, diluted with an equal volume of alcohol. The yellow plates which then separated were collected, dried, and analysed. (Found, $Pt=41{\cdot}18$. Calc., $Pt=41{\cdot}34$ per cent.)

The base was therefore methylamine.

Much of the expense entailed by this research has been met by grants from the Government Grant Committee of the Royal Society and from the Research Fund of the Chemical Society, for which we desire to express our indebtedness.

The Sorby Research Laboratory,
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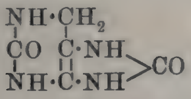
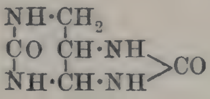
CXIX.—*A Synthesis of Tetrahydrouric Acid.*

By Edward Percy Frankland.

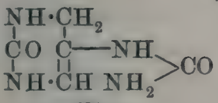
Tafel has shown (*Ber.*, 1901, **34**, 258) that the electrolytic reduction of uric acid on a lead cathode leads to the formation of three different substances in proportions varying with the experimental conditions, namely, purone (II), *iso*purone (III), and tetrahydrouric acid (IV) or (V):



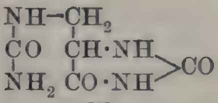
(I.)



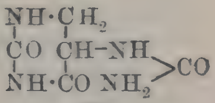
(II.)



(III.)



(IV.)



(V.)

Desoxyuric acid itself (I), probably the first step in the reduction, could not be isolated, and Tafel considered that this substance either was at once reduced further to purone or that it reacted with the elements of water to form tetrahydrouric acid, one of the rings opening in the process.

The present paper describes an attempt to synthesise this hypothetical desoxyuric acid, starting from $\alpha\beta$-diaminopropionic acid, $NH_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$. The monohydrobromide of this amino-acid, together with the requisite quantity of either hydrobromic or hydrochloric acid for the saturation of the second amino-group, was allowed to react in aqueous solution with a corresponding weight (two molecules) of potassium cyanate.

The resulting urea derivative was in general not isolated owing to the difficulty experienced in its purification; it was dissolved in 25 per cent. hydrochloric acid, and the solution evaporated in order to form the corresponding hydantoin. This proved to be a beautifully crystalline substance, soluble in water, giving a solution having an acid reaction towards litmus, and melting with decomposition and gas evolution at 216°. The results of an analysis indicated clearly that this substance was the intermediate stage towards desoxyuric acid, namely, tetrahydrouric acid, in which only one ring is closed with elimination of a molecule of water. The experiment thus resulted in the synthesis of tetrahydrouric acid, although the method was not such as to enable a decision to be made between the two possible formulæ (IV) and (V). These are based on Tafel's decomposition of tetrahydrouric acid with baryta (*Ber.*, 1901, **34**, 1182) (which yielded one molecule of diaminopropionic acid and two molecules of carbon dioxide), and are confirmed by the present synthesis:

$$NH_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H,HBr + HBr + 2KCNO =$$
$$2KBr + NH_2\cdot CO\cdot NH\cdot CH_2\cdot CH(NH\cdot CO\cdot NH_2)\cdot CO_2H,$$

(Not isolated.)

$$NH_2\cdot CO\cdot NH\cdot CH_2\cdot CH(NH\cdot CO\cdot NH_2)\cdot CO_2H =$$
$$H_2O + \text{Tetrahydrouric Acid.}$$

A portion of the tetrahydrouric acid thus obtained was dissolved in 25 per cent. hydrochloric acid, and the solution evaporated to a syrup, from which, by precipitating with alcohol, tetrahydrouric acid was recovered unchanged. Apparently the substance cannot be condensed to desoxyuric acid by this process.

The mother liquor from which the tetrahydrouric acid had been removed in the original preparation contained a syrupy substance, very soluble in water. This does not yield tetrahydrouric acid on further heating with hydrochloric acid, and it is possibly the hydantoin of a mono-urea derivative. Ellinger (*Ber.*, 1904, **37**, 335), as well as Neuberg and Silbermann (*Ber.*, 1904, **37**, 341), have shown that the β-amino-group in diaminopropionic acid hydrochloride or hydrobromide is very resistant to the action of nitrous acid; a similar observation was made by Tafel and E. P. Frankland (*Ber.*, 1909, **42**, 3138) in the case of the monohydrochloride of β-amino-α-methylaminopropionic acid, which yielded a mononitroso-derivative, the nitroso-group being presumably in the α-position. It is suggested that in these cases the β-amino-group may be shielded by internal salt formation with the carboxyl group. In the present instance it is possible that the amino-acid reacts less readily with the second molecule of cyanic acid, and this would account for the smallness of the yield of tetrahydrouric acid. This view is strengthened by experiments made by the author on αβ-dibenzylaminopropionic acid, in which case the reaction leads to the formation of a monourea derivative only. This compound can be converted quantitatively into a hydantoin, leaving a free amino-group, presumably in the β-position. The results of this work will be published in the near future.

EXPERIMENTAL.

The diaminopropionic acid used in the following experiments was prepared by the action of concentrated ammonia solution on αβ-dibromopropionic acid in sealed tubes at temperatures ranging from 80° to 155°.

The resulting hydrobromide, $NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H,HBr$, was purified by recrystallisation from water, and melted and decomposed at 238° (uncorr.). Klebs (*Ber.*, 1893, **26**, 2264; *Zeitsch. physiol. Chem.*, 1895, **21**, 309), who was the first to isolate this salt, gave 228—230° as the decomposition point. (Found, Br = 43·42. Calc., Br = 43·24 per cent.)

2·4 Grams of the above hydrobromide were dissolved in warm water with the addition of 6·15 grams of a 48 per cent. solution of hydrogen bromide, and treated with an aqueous solution of 4 grams of potassium cyanate. Considerable effervescence followed the mixing of the solutions. The mixture was kept for about an hour, and was then concentrated slowly to a small bulk. When the volume of the solution had been reduced to about 3 c.c., 10 grams of concentrated hydrochloric acid were added to the semicrystalline mass; the mixture was warmed for a few minutes, then allowed to cool, and the crystalline precipitate of potassium bromide collected by filtration and washed with concentrated hydrochloric acid. The filtrate and washings were concentrated to a syrupy mass on the water-bath, mixed with a little 25 per cent. hydrochloric acid, and evaporated almost to dryness on the water-bath. After boiling the residue with methyl alcohol, a further quantity of potassium bromide was filtered off; the total quantity obtained being 4·25 grams.

The methyl-alcoholic solution was evaporated nearly to dryness, and the residue dissolved with a small quantity of hot water. The solution was allowed to cool, and sown with crystals of tetrahydrouric acid obtained from a previous experiment. After a few minutes a crystalline precipitate separated; it was collected, washed with a small quantity of cold water, with absolute alcohol, and finally with ether. The weight of tetrahydrouric acid thus obtained was 0·58 gram. Another experiment, starting from 3·75 grams of the hydrobromide of diaminopropionic acid, yielded 1·25 grams of tetrahydrouric acid. The substance melted at 215° with gas evolution to a colourless liquid, was readily soluble in hot water, the solution having an acid reaction to litmus, only very sparingly soluble in absolute ethyl alcohol, and crystallised anhydrous from water in acicular prisms and hexagonal, prismatic plates.

For the purposes of analysis a specimen of the substance obtained by this method was recrystallised twice from water, and it melted and decomposed at 216°. Tafel gives 212—213° as the melting point of tetrahydrouric acid. (Found, $C=34·57$, $34·60$; $H=4·90$, $4·84$; $N=32·53$. Calc., $C=34·88$; $H=4·65$; $N=32·56$ per cent.)

Since the combustion of this substance in a vacuum appears to lead to the formation of an unusually high percentage of nitric oxide, thus giving percentages of nitrogen somewhat above what could be accounted for on the average experimental error (in two cases 33·10 and 32·94 per cent. respectively), in the above analysis the volume of nitrogen was corrected for nitric oxide in a gas apparatus.

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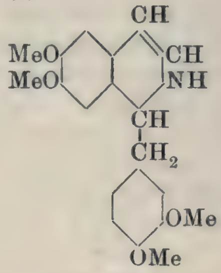
CXX.—iso*Quinoline Derivatives. Part V. The Constitution of the Reduction Products of Papaverine* (continued).

By Frank Lee Pyman and William Colebrook Reynolds.

In Part II of this series (Trans., 1909, **95**, 1610) it was shown by one of us that the amorphous base resulting from the reduction of papaverine is in reality tetrahydropapaverine, and it was further stated that Goldschmiedt's so-called "tetrahydropapaverine" is 1 : 2-dihydropapaverine (I):



(I.)

The reasons which led to this conclusion were as follows.

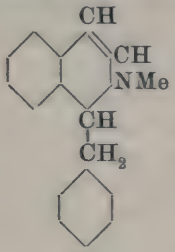
(1) Analyses and molecular weight determinations of the base and its derivatives prove that it has the formula $C_{20}H_{23}O_4N$, and its preparation by the reduction of papaverine, $C_{20}H_{21}O_4N$, therefore shows it to be a dihydropapaverine, unless it is obtained from an impurity in the papaverine, a possibility—at no time likely—which is definitely disproved in the present paper.

(2) The reactions of the base, for instance, the formation of a nitroso-derivative and benzoyl derivative, show that it contains an imino-group, therefore one of the additional hydrogen atoms occupies the 2-position of the *iso*quinoline ring.

(3) The resolution of the base by Pope and Peachey (Trans., 1898, **73**, 893) proves it to contain an asymmetric carbon atom, and on the assumption that this occupied the 1-position, as in alkaloids of the 1-benzyltetrahydro*iso*quinoline type (laudanosine, narcotine, etc.), the position of the remaining hydrogen atom was fixed, and the base designated 1 : 2-dihydropapaverine.

This base, however, was a compound of considerable stability, its reduction could not be effected, and its *N*-benzoyl derivative was not readily attacked either by bromine or by sulphuric acid and manganese dioxide; its behaviour therefore differed from that of

1-benzyl-2-methyl-1 : 2-dihydro*iso*quinoline (II) (Freund and Beck, *Ber.*, 1909, **42**, 1762), a compound which may readily be reduced



(II.)

to the corresponding tetrahydro*iso*quinoline, and which is easily attacked by oxidising agents.

This difference in behaviour was ascribed to the presence of a free imino-group in the former, and some corroboration of this view was adduced from the fact that Pictet and Athanasescu (*Ber.*, 1900, **33**, 2346), in preparing laudanosine by the reduction of papaverine methochloride, did not discover the *N*-methyl derivative of 1 : 2-dihydropapaverine. The present authors, however, now find that the reduction of papaverine methyl salts leads to the production not only of laudanosine, but also of a new base, $C_{21}H_{25}O_4N$, which is shown to be the *N*-methyl derivative of 1 : 2-dihydropapaverine. Further, the new base is as stable as the parent compound; its reduction cannot be effected either by tin and hydrochloric acid or by sodium and amyl alcohol. It is therefore clear that the difference in behaviour between 1-benzyl-2-methyl-1 : 2-dihydro*iso*quinoline and 1 : 2-dihydropapaverine is not merely due to the influence of the imino-group in the latter, and the assumption that this base has the constitution represented by the term 1 : 2-dihydropapaverine does not appear to be justified without further experimental evidence.

The further investigation of the constitution of this compound, however, more particularly with regard to the products obtained by its oxidation and degradation by complete methylation, is now in progress, and in order to avoid the use of a designation which may prove to be incorrect, it is proposed to adopt the name *pavine* for this base, $C_{20}H_{23}O_4N$, melting at 201—202°, which has been termed "tetrahydropapaverine" by Goldschmiedt (*Monatsh.*, 1886, **7**, 485; 1898, **19**, 324) and "1 : 2-dihydropapaverine" by Pyman (*loc. cit.*); the new base, $C_{21}H_{25}O_4N$, will therefore be N-*methylpavine*.

Pavine is always formed together with tetrahydropapaverine in the reduction of papaverine with tin and hydrochloric acid, and has been so obtained by different workers using papaverine having the correct melting point (Goldschmiedt, Pope and Peachey, Pyman), but the yield is only small, and varies from about 8 to 12 per cent. of the theoretical; it appeared therefore to be possible, although unlikely, that pavine was derived from some impurity in the papaverine. In order to settle this point, the commercial papaverine used in these experiments was on one occasion very carefully purified; on methylation and subsequent reduction, a quantity of *N*-methylpavine was obtained together with laudanosine, and it therefore follows that *N*-methylpavine is actually derived from *N*-methylpapaverine salts, and consequently that pavine is derived from papaverine.

N-Methylpavine is obtained by the reduction of papaverine methyl salts with tin and hydrochloric acid, together with laudanosine, from which it can be readily separated by either of two methods given in the experimental part of this paper; it is also formed to some extent in the oxidation of laudanosine with sulphuric acid and manganese dioxide. The relation between these alkaloids is therefore as follows:

$$\begin{tikzcd}
\text{Papaverine methosulphate} \arrow[rr, "+2H_2"] \arrow[dr, "+H_2"'] & & \text{Laudanosine} \arrow[dl, "-H_2"] \\
& \text{N-Methylpavine.} &
\end{tikzcd}$$

N-*Methylpavine hydriodide* and *methiodide* are also formed, together with *pavine hydriodide*, by the action of methyl iodide on pavine according to the equations:

$$C_{20}H_{23}O_4N + CH_3I = C_{21}H_{25}O_4N,HI$$

and

$$2C_{20}H_{23}O_4N + 2CH_3I = C_{20}H_{23}O_4N,HI + C_{21}H_{25}O_4N,CH_3I.$$

As in the case of pavine, so also in that of *N*-methylpavine, base and salts readily crystallise with a considerable amount of water of crystallisation.

EXPERIMENTAL.

Purification of Papaverine.

After a preliminary experiment, in which besides laudanosine a quantity of *N*-methylpavine was obtained by the reduction of papaverine methosulphate, the papaverine required for the next experiment was very carefully examined.

The base melted at 146—147°; it was converted into the hydrochloride, and this salt crystallised twice from water, being obtained in monoclinic plates, which decomposed at 231° (corr.); after regeneration, the base was converted into the hydrogen oxalate and the salt crystallised twice from alcohol, when it separated in fine rods, which decomposed at 199° (corr.); the base was then regenerated, but still melted at 146—147°, or 147—148° (corr.), and this melting point remained the same after recrystallisation of a specimen of the base from benzene.*

Reduction of Papaverine Methosulphate.

One hundred and eight-four grams of papaverine, which had been treated as above, were converted into the methosulphate (compare Decker and Pschorr, *Ber.*, 1904, **37**, 3401), and this was reduced with tin and hydrochloric acid in alcoholic solution, the conditions being similar to those previously adopted for the reduction of papaverine (Pyman, Trans., 1909, **95**, 1614). After decomposition of the tin salts with hydrogen sulphide, and removal of the tin sulphide, the liquor was precipitated with sodium carbonate, filtered from the crude laudanosine, and extracted with chloroform; the latter left on distillation a brown gum, which was dissolved in warm dilute hydrochloric acid; this solution, on cooling, deposited *N*-methylpavine hydrochloride in beautiful prisms. The crude laudanosine was purified by crystallisation as hydrogen oxalate, the mother liquors yielding, on regeneration of the base and crystallisation of this as hydrochloride, a further quantity of *N*-methylpavine. Altogether 152 grams of laudanosine and 9 grams of *N*-methylpavine hydrochloride were obtained.

The laudanosine obtained in this manner melts at 115—116° (corr.), and the melting point is unchanged after recrystallisation of the base from alcohol. The yield of pure laudanosine is therefore 78 per cent. of the theoretical; Pictet and Athanasescu (*loc. cit.*) obtained 50 to 60 per cent.

Laudanosine hydrogen oxalate crystallises from alcohol in microscopic needles, which contain $1\frac{1}{2}H_2O$, and, after drying at 100°, melts and decomposes at 163—165° (corr.), after sintering a few degrees earlier. After crystallisation from water, this salt contains $2\frac{1}{2}H_2O$, and melts to a turbid, viscous liquid at 80—82° (corr.). It is sparingly soluble in cold water or alcohol:

0·1532 † gave 0·3265 CO_2 and 0·0906 H_2O. C = 58·1; H = 6·6.

0·2009 † lost 0·0110 in a vacuum over H_2SO_4. H_2O = 5·5.

$C_{21}H_{27}O_4N,C_2H_2O_4,1\frac{1}{2}H_2O$ requires C = 58·2; H = 6·8; H_2O = 5·7 per cent.

0·1855 ‡ lost 0·0155 at 100°. H_2O = 8·4.

$C_{21}H_{27}O_4N,C_2H_2O_4,2\frac{1}{2}H_2O$ requires H_2O = 9·1 per cent.

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* In view of a recent publication by Pictet and Kramers (*Ber.*, 1910, **43**, 1329), it may be of interest to note that, on treatment of the purified papaverine with concentrated sulphuric acid, the crystals were, at first, superficially coloured violet, and then dissolved in the acid, giving a colourless solution.

† Air-dried salt (from alcohol). ‡ Air-dried salt (from water).

Separation of Laudanosine and N-*Methylpavine.*

That the above method for the separation of laudanosine and *N*-methylpavine is fairly complete is shown by the following experiment.

A mixture of 10 grams of laudanosine and 1 gram of *N*-methylpavine, when converted into acid oxalate and recrystallised from water, gave 12·2 grams of laudanosine hydrogen oxalate; the base regenerated from the mother liquors then crystallised as hydrochloride gave 1·2 grams of *N*-methylpavine hydrochloride; on again regenerating the base from the mother liquors and crystallising as acid oxalate, another 0·9 gram of laudanosine hydrogen oxalate was obtained, and the last mother liquors gave a base yielding a small quantity of hydrochloride, which was not further worked up; the quantities recovered were equivalent to 9·5 grams of laudanosine and 0·8 gram of *N*-methylpavine.

Another method for the separation of the two bases depends on the different solubilities of the bases in alcohol.

A mixture of 10 grams of laudanosine and 1 gram of methylpavine crystallised from a minimum of hot alcohol gave 8·9 grams of laudanosine; the remainder converted into hydrochloride and crystallised from water gave 1·5 grams of *N*-methylpavine hydrochloride, and after regenerating the bases from the final mother liquor and crystallising from alcohol, a further 0·3 gram of laudanosine was obtained; the quantities recovered were thus equivalent to 9·2 grams of laudanosine and 1·0 gram of *N*-methylpavine.

N-*Methylpavine*, $C_{21}H_{25}O_4N$.

This base is liberated in an amorphous condition when alkalis are added to aqueous solutions of its salts, but the precipitate becomes crystalline on keeping, and then forms colourless prisms, which, after thorough drying in the air, contain 1½ to 2½ H_2O. The hydrated base has no sharp melting point, but begins to soften at about 80°, gradually melts, and then effervesces at 100°; it loses nearly all its water of crystallisation when kept in a vacuum over sulphuric acid, and remains as a white, amorphous powder, which melts at about 90°:

0·4313 (air dried) lost 0·0380 in a vacuum over H_2SO_4. $H_2O = 8·8$.

$C_{21}H_{25}O_4N,2H_2O$ requires $H_2O = 9·2$ per cent.

0·1985 (dried in a vacuum) gave 0·5099 CO_2 and 0·1257 H_2O. $C = 70·1$; $H_2O = 7·1$.

After dehydration by boiling with benzene and anhydrous sodium sulphate, the base crystallises from benzene in hard prisms, which are anhydrous, and melt at 140—141° (corr.), after sintering a degree earlier; it crystallises from anhydrous ether in small, glistening prisms having the same melting point. It is sparingly soluble in water, ether, or light petroleum, but readily so in the other usual organic solvents. It dissolves in concentrated sulphuric acid, giving a pale yellowish-green solution:

0·1555 gave 0·4038 CO_2 and 0·0995 H_2O. C=70·8; H=7·2.
0·1514 „ 0·3922 CO_2 „ 0·0971 H_2O. C=70·6; H=7·2.
0·1865 „ 6·2 c.c. N_2 at 22° and 758 mm. N=3·8.
0·2090 „ by Zeisel's method, 0·5360 AgI. OMe=33·9.
0·1529 „ „ „ „ 0·3915 AgI. OMe=33·8.
$C_{21}H_{25}O_4N$ requires C=70·9; H=7·1; 4OMe=34·9; N=3·9 per cent.

The *hydrochloride* crystallises from water in large, colourless, well-formed prisms, which melt at 65—81° (corr.), and contain 8 molecules of water of crystallisation, of which 7½ are lost on drying first in a vacuum, and then at 100°. This salt is soluble in about 50 parts of cold water, but easily soluble in hot water or alcohol:

0·5121 (air dried) lost 0·1293 at 100°. H_2O=25·2.
$C_{21}H_{25}O_4N,HCl,8H_2O$, losing $7\frac{1}{2}H_2O$, requires H_2O=25·2 per cent.
0·1616 * gave 0·3707 CO_2 and 0·0972 H_2O. C=62·6; H=6·7.
0·1598 * „ 0·3664 CO_2 „ 0·0962 H_2O. C=62·5; H=6·7.
0·2124 * „ 0·0733 AgCl. Cl=8·5.
$C_{21}H_{25}O_4N,HCl,\frac{1}{2}H_2O$ requires C=62·9; H=6·8; Cl=8·8 per cent.

The *hydriodide* crystallises from water in large, nearly colourless prisms, which melt at 70—87° (corr.), and contain $6H_2O$. It is easily soluble in hot water or alcohol. After drying, it has no sharp melting point, but gradually softens from about 185° onwards:

0·2194 (air dried) lost 0·0412 at 100°. H_2O=18·8.
$C_{21}H_{25}O_4N,HI,6H_2O$ requires H_2O=18·3 per cent.
0·1704 * gave 0·3242 CO_2 and 0·0845 H_2O. C=51·9; H=5·6.
0·1892 * „ 0·0911 AgI. I=26·0.
$C_{21}H_{25}O_4N,HI$ requires C=52·2; H=5·4; I=26·3 per cent.

The *aurichloride* crystallises from a mixture of acetone and absolute alcohol in terra-cotta coloured needles, which contain a molecule of alcohol of crystallisation and decompose at 198° (corr.). It is almost insoluble in water or alcohol, but readily soluble in acetone:

0·2058 † gave 0·2824 CO_2 and 0·0764 H_2O. C=37·4; H=4·2.
0·1522 † „ 0·2086 CO_2 „ 0·0605 H_2O. C=37·4; H=4·5.

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* Dried at 100°. † Air-dried salt.

0·2287 * gave 0·0607 Au. Au = 26·5.

0·6416 * lost 0·0365 at 100°. $C_2H_6O = 5{\cdot}7$.

$C_{21}H_{25}O_4N,HAuCl_4,C_2H_6O$ requires C = 37·2; H = 4·4; Au = 26·6; $C_2H_6O = 6{\cdot}2$ per cent.

The *picrate* crystallises from water in small, glistening, yellow needles, which melt at 219° (corr.), after sintering slightly from 200°. It is very sparingly soluble in cold water or alcohol:

0·1576 * lost 0·0014 at 100°. $H_2O = 0{\cdot}9$.

0·1735 † gave 0·3532 CO_2 and 0·0754 H_2O. C = 55·5; H = 4·9.

$C_{21}H_{25}O_4N,C_6H_3O_7N_3$ requires C = 55·5; H = 4·8 per cent.

The *methiodide* separates in colourless, glistening rods, which contain $2H_2O$, and decompose at about 280° (corr.) on warming a methyl-alcoholic solution of the base with methyl iodide. It is sparingly soluble in cold water or hot alcohol:

0·5200 * lost 0·0353 at 100°. $H_2O = 6{\cdot}8$.

$C_{21}H_{25}O_4N,CH_3I,2H_2O$ requires $H_2O = 6{\cdot}8$ per cent.

0·1565 † gave 0·3036 CO_2 and 0·0792 H_2O. C = 52·9; H = 5·7.

0·2318 † ,, 0·1097 AgI. I = 25·6.

$C_{21}H_{25}O_4N,CH_3I$ requires C = 53·1; H = 5·7; I = 25·5 per cent.

After crystallisation from water, the methiodide forms beautiful, large, clear prisms, which contain $4H_2O$, and, after sintering from 114° and gradually becoming viscous, effervesce at 118—119° (corr.); after drying the fully hydrated salt at 100°, it has no sharp melting point, but begins to sinter at about 165° (corr.), and gradually becomes viscous and effervesces on raising the temperature:

0·1529 * gave 0·2607 CO_2 and 0·0884 H_2O. C = 46·5; H = 6·5.

0·2030 * ,, 0·0830 AgI. I = 22·1.

0·2716 * lost 0·0326 at 110°. $H_2O = 12{\cdot}0$.

$C_{21}H_{25}O_4N,CH_3I,4H_2O$ requires C = 46·4; H = 6·4; I = 22·3; $H_2O = 12{\cdot}7$ per cent.

The *methochloride* was prepared from the methiodide by double decomposition with silver chloride. It crystallises from water in beautiful, colourless prisms, which are sparingly soluble in water, and melt at 75—99° (corr.). The air-dried salt contains $7H_2O$, of which 6½ are lost at 100°; the dried salt sinters at 150—170°, and then effervesces:

0·5173 * lost 0·1161 at 100°. $H_2O = 22{\cdot}4$.

$C_{21}H_{25}O_4N,CH_3Cl,7H_2O$, losing $6\frac{1}{2}H_2O$, requires loss = 22·0 per cent.

0·1528 † gave 0·3599 CO_2 and 0·0987 H_2O. C = 64·3; H = 7·2.

$C_{21}H_{25}O_4N,CH_3Cl,\frac{1}{2}H_2O$ requires C = 63·7; H = 7·1 per cent.

The *methohydroxide* was prepared by digesting a hot aqueous solution of the methiodide with silver oxide, filtering from silver iodide, and evaporating the liquor until crystals formed on the surface. On cooling, the base separated in large, transparent prisms, which melted and effervesced at about 100°. It contains a large and variable amount of water of crystallisation. It is very easily soluble in water, giving a strongly alkaline solution, which yields with aqueous potassium iodide a precipitate of the methiodide.

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* Air-dried salt. † Dried at 100°.

Methylation of Pavine.

Ten grams of pavine were dissolved in about 50 c.c. of chloroform, and gently warmed with 10 grams of methyl iodide, until a reaction set in. A dark oil was deposited, and on keeping overnight, this became a mass of crystals, which were collected, washed with alcohol, and fractionally crystallised, first from absolute alcohol and then from water. The following products were obtained.

(1) 3·5 Grams of *N*-methylpavine methiodide. This salt effervesced at 118—119° (corr.), and its melting point suffered no depression when the salt was mixed with the pure substance:

0·1636 * gave 0·2819 CO_2 and 0·0931 H_2O. C = 47·0; H = 6·4.
0·2063 * lost 0·0252 at 100°. H_2O = 12·2.
$C_{21}H_{25}O_4N,CH_3I,4H_2O$ requires C = 46·4; H = 6·4;
H_2O = 12·7 per cent.

(2) 7·0 Grams of *N*-methylpavine hydriodide. This salt melted at 70—87° (corr.), and its melting point suffered no depression when the salt was mixed with the pure substance:

0·1535 * gave 0·2374 CO_2 and 0·0892 H_2O. C = 42·2; H = 6·5.
0·2045 * lost 0·0374 at 100°. H_2O = 18·3.
$C_{21}H_{25}O_4N,HI,6H_2O$ requires C = 42·6; H = 6·5; H_2O = 18·3 per cent.

(3) 0·8 Gram of *pavine hydriodide*. This salt softened about 75°, but did not melt until about 265°. After drying at 100°, it softens together at 195° (corr.) without really melting, and its melting point suffered no depression when the salt was mixed with the pure substance prepared by neutralising pavine with hydriodic acid. This salt contains about $4H_2O$, and is sparingly soluble in cold water.

(*a*) Salt obtained in the methylation:
0·1967 * lost 0·0276 first in a vacuum, then at 100°. H_2O = 14·0.
0·1578 † gave 0·2950 CO_2 and 0·0740 H_2O. C = 51·0; H = 5·3.

(*b*) Salt obtained by neutralising pavine with hydriodic acid:
0·2013 * lost 0·0228 first in a vacuum, then at 100°. H_2O = 11·3.

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* Air-dried salt. † Dried at 100°.

0·1546 * gave 0·2901 CO_2 and 0·0735 H_2O. C = 51·2; H = 5·3.
$C_{20}H_{23}O_4N,HI,3H_2O$ requires $H_2O = 10·3$ per cent.
$C_{20}H_{23}O_4N,HI,4H_2O$ „ $H_2O = 13·3$ „
$C_{20}H_{23}O_4N,HI$ requires C = 51·2; H = 5·2 per cent.

A number of small fractions consisting of mixtures of the above were also obtained.

THE WELLCOME CHEMICAL WORKS,
DARTFORD, KENT.

CXXI.—*The Specific Rotatory Power of Hyoscyamine and the Relation between that of Alkaloids and their Salts.*

By FRANCIS HOWARD CARR and WILLIAM COLEBROOK REYNOLDS.

IN a recent communication Barrowcliff and Tutin (Trans., 1909, **95**, 1966) have given $[\alpha]_D$ ± 32·1° for the specific rotatory power of optically pure *d*- and *l*-hyoscyamine, deriving this figure by calculation from the values they obtained for the pure *d*- and *l*-hyoscyamine *d*-camphorsulphonates in aqueous solution. This, being considerably higher than the figure generally accepted for *l*-hyoscyamine, namely, $[\alpha]_D$ − 21°, led them to conclude that no optically pure hyoscyamine had hitherto been obtained, and they attributed the discrepancy to unavoidable racemisation occurring in the process of the regeneration of the base.

By fractional crystallisation of a quantity of base having $[\alpha]_D$ about − 20°, however, they obtained a fraction having $[\alpha]_D$ − 25·8°, and this was the highest rotatory power observed.

It has been shown by Cushny and confirmed by Laidlaw that *d*- and *l*-hyoscyamine differ very considerably in their physiological properties, the lævo-isomeride being the more active. The question therefore of the specific rotatory power of pure *l*-hyoscyamine assumes considerable practical importance, for, according to the position defined by Barrowcliff and Tutin, the commercial product in general use is not the pure *l*-base possessing the highest possible physiological activity, but a mixture containing a considerable amount of the racemic base—atropine. Since the rotatory power of hyoscyamine affords the best means of determining its purity, no uncertainty must exist about the correctness of this constant.

In the course of extended experience in the preparation of

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* Dried at 100°.

l-hyoscyamine, we have uniformly observed the specific rotatory power, of what we considered the pure base, to be about $[\alpha]_D - 21^\circ$ (in dilute alcohol). By prolonged fractional crystallisation of both the camphorsulphonate and the alkaloid, we have not been able to obtain a base having a higher directly determined specific rotatory power than $[\alpha]_D - 22{\cdot}0^\circ$ (in dilute alcohol). That the latter was pure *l*-hyoscyamine was proved beyond all question by the following facts:

(1) When the base of directly determined specific rotatory power $[\alpha]_D - 22{\cdot}0^\circ$ (in dilute alcohol) was neutralised, the value calculated as basic ion rose to $[\alpha]_D - 32{\cdot}5^\circ$ (in aqueous solution), a figure almost identical with that deduced by Barrowcliff and Tutin.

(2) It gave a *d*-camphorsulphonate, which, without purification, had $[\alpha]_D - 7{\cdot}7^\circ$, again a value almost identical with that observed by Barrowcliff and Tutin for the salt on the specific rotatory power of which they founded their conclusions.

There remains to be explained the observation by Barrowcliff and Tutin of $[\alpha]_D - 25{\cdot}8^\circ$ (in dilute alcohol) for the specimen of *l*-hyoscyamine obtained by fractional crystallisation. In regard to this, these authors have very kindly furnished us with particulars of their procedure, which now admits, in view of our own observations as to the behaviour of *l*-hyoscyamine, of a perfectly simple explanation of their result. It appears that in determining the specific rotatory power of the specimen of base in question there was introduced into the alcohol (previously distilled over potassium hydroxide) with which the solution was prepared, a small amount of acetic acid, with the object of counteracting any slight alkalinity, which might be expected to increase the rate of racemisation. The resulting solution therefore probably contained a partly neutralised base, and in consequence gave a higher rotation than would have been the case if only free base had been present.

It also follows from the above-mentioned facts that hyoscyamine does not, after all, possess any considerable susceptibility to racemisation, such as Barrowcliff and Tutin attributed to it.

We consider that there is no doubt whatever that the specific rotatory power of optically pure *l*-hyoscyamine is $-22{\cdot}0^\circ$ (in 50 per cent. alcohol).

It is evident that Barrowcliff and Tutin arrived at an erroneous conclusion by assuming that the specific rotatory power of the basic ion, deduced from the molecular rotation of its salts in a dissociating solvent, would be identical, or nearly so, with that directly determined for the base, also in a dissociating solvent. Although this assumption may be legitimate in the case of many bases, there exists evidence to indicate that it is not invariably so, particularly for tertiary bases, in which class are most of the naturally occurring alkaloids. For example, most of the alkaloids of the aconitine group are dextrorotatory, but their salts are lævorotatory, whilst quinine and cocaine have each a lower specific rotatory power than their respective salts. It must not be overlooked, however, in regard to most of these cases that owing to differences of solubility of base and salt the published rotations of the former were made in alcohol of 90—100 per cent., whilst aqueous solutions of the salts were employed. From this it might be argued that the differences observed were attributable to incomplete ionisation in the case of the bases. Aconine and *l*-hyoscine afford instances not open to this objection, the former having $[\alpha]_D + 23{\cdot}0°$ as base, and $[\alpha]_D - 8{\cdot}8°$ as salt, and the latter $[\alpha]_D - 28{\cdot}0°$ as base, and $[\alpha]_D - 32{\cdot}8°$ as salt, the determinations being made in aqueous solution in every case.

We believe that the distinction between the specific rotatory power of a base determined directly in a dissociating solvent and that deduced for the basic ion from a determination of a salt has not been sufficiently appreciated. We have therefore considered it desirable to extend the investigation to a number of other alkaloids with the object of further supporting our contention as to the incorrectness of the principle above-stated.

The alkaloids investigated were, besides hyoscyamine, the following: cocaine, codeine, hydrastine, nicotine, and quinine. The specific rotatory values of these were determined as base and basic ion in the same dissociating solvent, which was either water or 50 per cent. alcohol, the former being used wherever the base was sufficiently soluble in it. The comparisons showed that all these bases without exception behave similarly to hyoscyamine, the two values obtained differing widely, as can be seen from the following table:

Alkaloid.	Solvent.	$[\alpha]_D$ of base (direct determination).	$[\alpha]_D$ of basic ion in solution of a salt.
Codeine	Water	$-144{\cdot}4$	$-133{\cdot}8$
Nicotine	,,	$-78{\cdot}0$	$+23{\cdot}1$
Hydrastine	50 % alcohol	$+115{\cdot}0$	$+197{\cdot}4$
Cocaine	,, ,,	$-35{\cdot}4$	$-77{\cdot}7$
Quinine	,, ,,	$-170{\cdot}5$	$-262{\cdot}1$

We have also observed that whilst the specific rotatory power of the *l*-hyoscyamine basic ion in aqueous solution (as a salt) was $[\alpha]_D - 32{\cdot}5°$, the value in 50 per cent. alcoholic solution was only $[\alpha]_D - 27{\cdot}0°$. Although the work of many investigators, notably Pope and Peachey (Trans., 1899, **75**, 1066), has shown that the rotation of a base is very considerably altered by the nature of the solvent, it might be supposed that water and 50 per cent. alcohol, being dissociating solvents, would act alike. Since the values for hyoscyamine salts in water and in 50 per cent. alcohol differ somewhat widely, a similar comparison was made of other alkaloids and their salts, and it was shown that the respective values differ very considerably in almost every case. It follows that although 50 per cent. alcohol is a dissociating solvent, it must not be regarded as having the same influence upon the rotation as water. An attempt to trace the influence which the solvent is thus shown to exert upon the specific rotatory power of a number of bases and salts has led to some interesting results, which are recorded in the experimental part of this paper.

From the results obtained as to the influence of acids on the specific rotatory power of alkaloids of known constitution in dissociating solvents, it would appear that the differences cannot be attributed to structural change, and we suggest that the free alkaloids are either not ionised in solution at all, or only partly so, and that, whereas the basic nitrogen has a quinquevalent function in the salts, in the base it functions as tervalent even in aqueous solution. In other words, such bases do not form quaternary hydroxides with water as do ammonia and simple substituted ammonium bases.

EXPERIMENTAL.

The Specific Rotatory Power of Hyoscyamine.

l-Hyoscyamine *d*-camphorsulphonate was frequently recrystallised from acetone until no further change of melting point or specific rotation was effected; the base was then regenerated with ammonia and rapidly extracted with chloroform, the chloroform solution washed first with dilute ammonia and then with water, and evaporated in a vacuum at a low temperature. The base thus obtained, which gave $[\alpha]_D -21\cdot7°$ in 50 per cent. alcohol, was recrystallised twelve times from light petroleum (b. p. 80—120°). It melted at 107—108°.

One gram, made up to 25 c.c. with 50 per cent. alcohol, gave, in a 2-dcm. tube, $\alpha_D -1\cdot765°$, whence $[\alpha]_D -22\cdot06°$.

Since, during the last six crystallisations, the specific rotatory power was only increased by 0·1°, this substance must be regarded as pure. During the recrystallisation evidence was obtained of dimorphism, there being, in addition to the ordinary form, denser and larger crystals melting at 102°, which spontaneously change on heating to those having the higher melting point.

The rotation of hyoscyamine is not affected by the degree of concentration.

Four grams, made up to 20 c.c. with 50 per cent. alcohol, gave, in a 1-dcm. tube, α_D −4·41°, whence $[\alpha]_D$ −22·0°.

The Specific Rotatory Power of l-*Hyoscyamine Basic Ion.*

The specific rotatory power of *l*-hyoscyamine basic ion was determined by observing the rotation of the base dissolved in several dilute acids to neutrality. The results given in the following table show, as was of course expected, that the value for the basic ion is independent of the acid used:

l-Hyoscyamine of $[\alpha]_D$ −22° neutralised with	Grams per 100 c.c.	Length of tube.	$[\alpha]_D$.	$[\alpha]_D$ of basic ion.
Sulphuric acid	4·015	2-dcm.	−2·62	−32·6
Sulphurous acid.........	4·009	,,	−2·60	−32·4
Hydrochloric acid	4·0	,,	−2·59	−32·4
Acetic acid	4·0	,,	−2·6	−32·5

The Specific Rotatory Power of d-*Hyoscyamine.*

Some *d*-hyoscyamine was prepared from atropine by fractionally crystallising the *d*-camphorsulphonate in the manner described by Barrowcliff and Tutin (*loc. cit.*), and it was found that the rotations of the base and its neutral solutions agree with those recorded for the *l*-base, excepting that being more difficult to obtain quite free from the racemic form, the figures are somewhat lower than those observed for the latter.

One gram, made up to 25 c.c. with 50 per cent. alcohol, gave, in a 2-dcm. tube, α_D +1·68°, whence $[\alpha]_D$ +21°; 1 gram, neutralised with sulphuric acid and made up to 25 c.c., gave, in a 2-dcm. tube, α_D +2·50°, whence $[\alpha]_D$ +31·25°.

The Effect of Concentration on the Specific Rotatory Power of l-*Hyoscyamine* d-*Camphorsulphonate.*

It has been found that the rotation of pure *l*-hyoscyamine *d*-camphorsulphonate decreases as the concentration increases, as shown by the following results:

l-*Hyoscyamine* d-*Camphorsulphonate.**

Grams per 100 c.c.	Length of tube.	α_D.	$[\alpha]_D$.	$[M]_D$.
20	2-dcm.	−2·10	−5·25	−27·35
16	,,	1·97	6·16	32·1
12	,,	1·62	6·75	35·16
8	,,	1·20	7·50	39·07
4	,,	0·67	8·38	43·65

These results, when plotted, form a straight line, from which the specific rotatory power at the point of greatest dilution is found to be $[\alpha]_D$ −9·1°, whence $[M]_D$ −47·4°.

As shown in the concluding part of this paper, this salt has a dextrorotation in chloroform solution, giving $[M]_D$ +9·9°.

Non-racemisation of the Base during Regeneration.

The following experiment was carried out in order to see to what extent racemisation occurs during the process of regenerating hyoscyamine. Some hyoscyamine camphorsulphonate, which gave $[\alpha]_D$ −7·2° in 7·5 per cent. aqueous solution, was converted into the base by the method previously described. The base gave $[\alpha]_D$ −22·3° in 50 per cent. alcohol. One gram of this base was combined with the quantity of *d*-camphorsulphonic acid which by previous titration was found to be required (owing to the fact that *d*-camphorsulphonic acid retains water of crystallisation, this procedure was necessary), namely, 0·8408 gram, and made up to 25 c.c., making a solution equivalent to 1·803 grams of *l*-hyoscyamine *d*-camphorsulphonate in 25 c.c. This solution gave, in a 2-dcm. tube, α_D −1·11°, whence $[\alpha]_D$ −7·7°. It is thus proved that the alkaloid suffered no loss of rotatory power during the process.

The Influence of Neutralisation on the Specific Rotatory Power of Alkaloids.

The change of specific rotatory power, which is brought about when an alkaloid is neutralised, was determined in several instances, employing the same solvent for both base and salt. The results, which are recorded in the table on p. 1335, show that the rotation is sometimes increased and sometimes diminished, there being a change in every case which we have investigated.

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* Barrowcliff and Tutin (*loc. cit.*), in calculating the specific rotatory power of *d*- and *l*-hyoscyamine from the above salt, employed the figure $[M]_D$ +51° for the molecular rotatory power of the *d*-camphorsulphonic ion. Pope and Peachey (Trans., 1899, **75**, 1066) gave $[M]_D$ +51·7°; but in a private communication, Prof. Pope informs us that more recent determinations have afforded a somewhat lower result. From a large number of determinations of the specific rotatory power of pure ammonium camphorsulphonate, we have obtained as a mean result $[\alpha]_D$ +20·1°, whence $[M]_D$ +50·05°, but this figure is subject to considerable variation according to the temperature.

The Influence of the Solvent on the Specific Rotatory Power of Alkaloids.

Owing to the insolubility of many alkaloids in water, 50 per cent. alcohol has been employed in determining the rotations of the insoluble ones. In order to determine whether this solvent may be regarded as having the same effect as water, comparisons have been made employing water and 50 per cent. alcohol for dissolving the alkaloids or salts. The differences, which in some cases are considerable, are given in tabular form:

	Solvent: Water.				Solvent: 50 per cent. alcohol.				
	Length of tube.	Grams per 100 c.c.	α_D.	$[\alpha]_D$.	Length of tube.	Grams per 100 c.c.	α_D.	$[\alpha]_D$.	Diff. of $[\alpha]_D$.
Cocaine neutralised with H_2SO_4	2-dcm.	1·088	−1·78	−81·8	2-dcm.	1·088	−1·69	−77·7	4·1
Hydrastine neutralised with HCl	,,	2·0	+6·32	+158·0	,,	1·643	+6·47	+197	39·0
l-Hyoscyamine neutralised with H_2SO_4 …………	,,	4·015	−2·62	−32·6	,,	4·0	−2·16	−27·0	5·6
Nicotine ………	,,	4·795	−7·47	−77·9	,,	4·368	−9·10	−104·2	26·3
Quinine neutralised with H_2SO_4	,,	4·0	−22·11	−276·4	,,	4·0	−20·97	−262·1	14·31

Since the addition of an equal weight of alcohol to the water modifies the specific rotatory power, the addition of larger proportions might be expected to produce further change.

Hydrastine, which has a strong dextrorotation in 50 per cent. alcohol, is optically inactive in 95 per cent. alcohol, and lævorotatory in 100 per cent. alcohol; a similar change occurs when acetone is employed as the solvent.

A striking experiment bearing on this point is recorded in the following table:

Hydrastine.

Solvent.	Length of tube.	Concentration.	α_D.	$[\alpha]_D$.
50 per cent. alcohol……	2-dcm	0·204	+0·47	+115·0
85 ,, ,, ……	,,	0·2	+0·15	+37·5
93 ,, ,, ……	,,	0·2	+0·12	+30·0
95 ,, ,, ……	,,	0·4	0·0	0·0
97 ,, ,, ……	,,	0·4	−0·10	−12·5
100 ,, ,, …… (Coml. abs.)	,,	0·291	−0·29	−49·8
50 per cent. acetone …	,,	0·2	+0·40	+100·0
Acetone (coml. pure) …	,,	4·0	−6·80	−85·0

Alkaloid.	Free base.					Basic ion in solution of a salt.					Arithmetical difference of $[M]_D$ of base and salt.
	Solvent.	Grams per 100 c.c.	a_D.	$[a]_D$.	$[M]_D$.	Weighed as	Grams of base per 100 c.c.	a_D.	$[a]_D$.	$[M]_D$.	
Cocaine	50% alcohol	1·088	-0·77	-35·4	-107·3	Hydrochloride calculated as base	0·3569	-5·60	-78·5	-238·0	130·7
Codeine	Water	0·8	-2·31	-144·4	-431·8	Base neutralised by HCl	2·0	-5·35	-133·8	-400·0	31·8
Hyoscyamine ...	50% alcohol	4·0	-1·765	-22·0	-63·6	Base neutralised by H_2SO_4	4·0	-2·16	-27·0	-78·0	14·4
Hydrastine......	50% alcohol	0·204	+0·47	+115·2	+442	Hydrochloride calculated as base	1·643	+6·47	+197·0	+754·0	312·0
Nicotine	Water	4·795	-7·47	-77·9	-126·2	Base acidified by H_2SO_4	4·96	+2·29	+23·1	+37·4	163·6
Quinine	50% alcohol	4 0	-13·64	-170 5	-552·1	Base neutralised by H_2SO_4	4·0	-20·97	-262·1	-849·0	297 0

Taken in a 2-dcm. tube. The salts and bases were all employed in the anhydrous condition.

Modifying Influence of Different Acidic and Basic Groups on the Specific Rotatory Power of Bases and Acids in Dry Chloroform.

The molecular rotatory power of an alkaloid and its different salts in anhydrous chloroform, where dissociation cannot occur, might be expected to vary, since the salt remains in the molecular condition. Such is shown to be the case. Where different acids are employed to neutralise the base, the rotation value differs. The results recorded in the following table bear upon this point:

Comparison of the Specific Rotation of Alkaloids and their Salts in Dry Chloroform, 1 = *2-dcm.*

	Free base.				Anhydrous salt.			
Alkaloid.	Grams per 100 c.c.	α_D.	$[\alpha]_D$.	$[M]_D$.	Weighed as	Grams per 100 c.c.	α_D.	$[M]_D$.
Cocaine	4	−1·26	−15·75	−47·7	Hydrochloride	2	−2·30	−193·8
Hyoscyamine	4	−1·90	−23·75	−68·7	Base neutralised by HCl and dried	4	−2·78	−100·2
Hydrastine..	2	−2·55	−63·8	−244·3	Hydrochloride	2	+8·52	+893
					Sulphate	2	+7·44	+803
					Acid oxalate...	2	+8·22	+972

The above results point to the modifying influence which the presence of different acid groups has on the rotation value of the asymmetric carbon atom of the base. A similar influence is produced on the asymmetric carbon atom of the acid by combination with different bases. This has been proved by determining the rotatory power in dry chloroform of the active and inactive camphorsulphonates of various alkaloids and taking the difference. This method affords a means of determining what proportion of the optical activity of the active salt of an active base is due to the respective basic and acidic parts of the molecule. The observations referred to are recorded in the following table:

	$[M]_D$ in chloroform.		
Camphorsulphonates of	Salt of *d*-acid.	Salt of *dl*-acid.	Difference due to *d*-camphorsulphonic complex.
Codeine	−50·5	−202·7	152 2
Cocaine	−99·1	−228·0	128·9
l-Hyoscyamine ...	+9·9	−107·0	116·9
Atropine	+114·2	0·0	114·2
Hydrastine	+962·0	+791·0	171·0
Papaverine	+150·0	0·0	150·0

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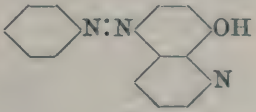
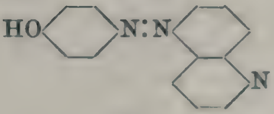
CXXII.—p-*Hydroxyazo-derivatives of Quinoline.* *Part I.*

By JOHN JACOB FOX.

THE hydroxyazo-derivatives of 8-hydroxyquinoline are of especial interest, as they contain a fairly basic group in the ortho-position with respect to the hydroxyl group. It was expected that this would have a profound effect on the acidic properties of the hydroxyazo-compounds obtained. As a matter of fact, none of the compounds containing the hydroxyl group in the quinoline nucleus could be acetylated even after prolonged boiling with acetic anhydride and anhydrous sodium acetate, and it was not found possible to prepare the methoxy-derivatives by boiling with methyl iodide and sodium methoxide. Monohydrochlorides could be readily prepared, but the dihydrochlorides to which the oxonium salt structure is attributable (Hewitt and Fox, Trans., 1908, **93**, 333) were very unstable, and could only be preserved in an atmosphere of hydrogen chloride. In all these respects the compounds differ strikingly from the simple hydroxyazo-compounds, such as benzeneazophenol or benzeneazo-α-naphthol. In order to ascertain whether the basic character of the quinoline nucleus affected the molecule as a whole, or whether the presence of the basic group in the ortho-position with respect to the hydroxyl group was the factor which prevented acetylation and alkylation of the hydroxyl group in the 8-position, compounds were prepared in which the hydroxyl group was no longer in the quinoline nucleus. The simplest of the two kinds of compounds are indicated by the formulæ:


(I.)


(II.)

Whilst the compound represented by formula I could not be acetylated even when dissolved in pyridine, compound II was found to undergo acetylation and alkylation with ease, as is the case with benzeneazophenol. The only explanation of the circumstance which appears to meet all the facts is that the hydroxyl group in I is prevented from exerting its normal activity by the presence of the strongly basic group in its neighbourhood.

The possibility of the compounds being quinonehydrazones would not agree with the observed behaviour, since then acetylation and alkylation should take place readily. The instability of the dihydrochloride of the type I, as compared with that of type II, is better explained as due to the formation of oxonium salts rather than carbonium salts, for if stable carbonium salts can be formed in II by the carbon atom, in the benzene nucleus para- with respect to the azo-grouping, there appears to be no reason why even more stable salts should not also be formed by I.

Both types of substance are true hydroxyazo-compounds, judging from the absorption spectra of the solutions in alcohol; for although some variation in the persistency of the main band occurs (curve, p. 1348), the head of this band, both with 5-benzeneazo-8-hydroxyquinoline and quinolineazophenol, occurs at about $1/\lambda$ 2600, just as in the case of aminobenzeneazophenol (Hewitt and Thomas, Trans., 1909, **95**, 1295), which also contains a basic group in the molecule. In the extreme case of a basic hydroxyazo-compound, such as quinolineazohydroxyquinoline, the absorption spectrum still gives the head of the band at $1/\lambda$ 2500 about, although the persistency is much diminished (curve, p. 1348). A consideration of the properties of the series of compounds described (for example, the formation of dihydrochlorides and hydrates, the colours obtained by dissolving in strong mineral acids and the position of the heads of the main bands in the absorption spectra) shows that even in these compounds, in which from the presence of the basic quinoline nucleus the possibility of quinone-hydrazone formation was increased, no such change from the true hydroxyazo-structure had taken place.

EXPERIMENTAL.

The *p*-hydroxyazo-derivatives of quinoline described here were prepared in the usual way from the diazonium chlorides and solutions of 8-hydroxyquinoline in aqueous sodium hydroxide. Mathëus stated that he had prepared benzeneazohydroxyquinoline, *p*-tolueneazohydroxyquinoline, and *p*-bromobenzeneazohydroxyquinoline (*Ber.*, 1888, **21**, 1642), but it was impossible to repeat the work from his description, as no melting points are given, and the properties of the substances are inadequately described. I therefore prepared these three derivatives amongst the others, and descriptions will be found below. All the azo-derivatives of 8-hydroxyquinoline gave sparingly soluble sodium salts, which separated from the alkaline solutions after some hours. It was necessary to allow the combination to proceed for twelve hours or longer, as otherwise some unchanged hydroxyquinoline was obtained. The fact that the sodium salt of 8-hydroxyquinoline is hydrolysed to a greater extent than that of phenol (this vol., p. 1119) is doubtless the cause of the slow combination. The insolubility of the sodium salts furnished a ready method of purifying the hydroxyazo-compounds, as any unchanged substance would remain in solution in the alkaline liquid.

5-*Benzeneazo*-8-*hydroxyquinoline.*

The benzenediazonium chloride solution, prepared from 14·7 grams of aniline, was poured into an aqueous sodium hydroxide solution containing 22 grams of 8-hydroxyquinoline. After eighteen hours the insoluble red sodium salt was collected, washed with water, decomposed with dilute acetic acid, washed with water, dried, and powdered. The powdered material crystallised best from alcohol in clusters of needles of chocolate-brown colour (m. p. 171°). The compound dissolved in chloroform, pyridine, benzene, and the usual organic solvents:

0·2144 gave 0·5668 CO_2 and 0·0898 H_2O. C = 72·1; H = 4·65.
0·1760 „ 26·0 c.c. N_2 at 20° and 764 mm. N = 17·2.
$C_{15}H_{11}ON_3$ requires C = 72·3; H = 4·4; N = 16·9 per cent.

Some of the powdered material was mixed with anhydrous sodium acetate and boiled for several hours with acetic anhydride; the product was poured into alcohol, diluted with water after some time, and the precipitate collected and washed. The crude product did not melt sharply, but on recrystallising twice from alcohol it melted at 170°, and when mixed with the original substance showed no depression of melting point. Similar results were obtained when a pyridine solution of the substance was boiled with acetic anhydride. It is clear that if any acetylation occurs, the acetyl derivative formed is very small in amount, for the main quantity of material is recovered unchanged.

An attempt was made to methylate the compound by heating a solution in methyl alcohol, containing sodium methoxide, with methyl iodide. The product obtained crystallised from alcohol, and melted at 170°; when mixed with the original substance, no change in melting point was observed. The experiment was repeated with the silver salt; but although in this case the crude product softened at a lower temperature than the melting point, recrystallisation from alcohol again yielded the original material. As this suggested considerable hydrolysis of the salts, the sodium salt was prepared. It was not possible to obtain this salt pure, since the neutral salt was hydrolysed by water, and a determination of sodium gave only about 90 per cent. of the required amount. The *silver* salt was prepared by dissolving the compound in the calculated amount of alcoholic sodium hydroxide, and adding an alcoholic solution of silver nitrate. A purple salt was precipitated, which was collected, washed with water, and then with hot alcohol. It became much darker on washing with alcohol, and yielded an amount of silver considerably in excess of that required for the neutral salt, indicating that the salt had been decomposed by the alcohol and the acid removed, leaving excess of silver.

It was important to examine the salts of benzeneazohydroxyquinoline acting as a base in order to ascertain whether salts of the normal "ammonium" type were formed, and some of these were prepared. The hydrochloride was prepared by evaporating a solution of the base in concentrated hydrochloric acid until crystals formed. After setting aside for some time, the crystals were collected, and washed with a little strong acid. The *hydrochloride* was obtained as a mass of dark red needles, but, if concentrated too rapidly, as an almost black, crystalline mass of plates, melting at 223°. The substance retains all its hydrogen chloride at 100°:

0·2482 gave 0·1258 AgCl. Cl = 12·5.

$C_{15}H_{11}ON_3,HCl$ requires Cl = 12·4 per cent.

The *zinc* salt was obtained by evaporating a solution of the hydrochloride with excess of hydrochloric acid and zinc chloride until crystals began to form; these consisted of dark red needles:

0·2736 gave 0·0302 ZnO. Zn = 8·9.
0·2058 ,, 0·1588 AgCl. Cl = 19·1.

$(C_{15}H_{11}ON_3,HCl)_2,ZnCl_2$ requires Zn = 9·2; Cl = 20·6 per cent.

This salt is probably hydrated.

Platinichloride.—An alcoholic solution of the hydrochloride was mixed with a solution of chloroplatinic acid. A dark, chocolate-coloured, microcrystalline precipitate formed:

0·3446 gave 0·0752 Pt. Pt = 21·8.

$(C_{15}H_{11}ON_3)_2,H_2PtCl_6$ requires Pt = 21·5 per cent.

The dihydrochloride could not be isolated from a solution in chloroform, for, although a dark purple precipitate resulted on leading in hydrogen chloride, the salt fumed strongly in the air, and analysis showed that the final product did not contain sufficient chlorine for the dihydrochloride. The salt is therefore much more unstable than the corresponding derivatives of benzeneazo-α-naphthol, and was finally prepared by passing hydrogen chloride over a weighed quantity of substance in a stoppered tube and determining the increase of weight, the apparatus being weighed full of hydrogen chloride before and after passing in the gas. The resulting salt was dark violet, almost black:

0·1606 benzeneazohydroxyquinoline absorbed 0·0488 HCl.
Increase = 30·4.
$C_{15}H_{11}ON_3$ requires increase = 28·3 per cent.

As stated above, this salt fumes in the air, and the loss of weight was only about three-quarters of that required for a loss of one molecule of hydrogen chloride; it was found that this was due to the formation of a hydrate in moist air, and in this respect the substance behaves like other hydroxyazo-compounds (Hewitt, *Ber.*, 1895, **28**, 799):

0·1606 gave 0·1900 substance after being subjected to action of hydrogen chloride, and keeping all night in moist air; AgCl obtained from this = 0·0932. Cl = 12·1.
$C_{15}H_{11}ON_3,HCl,\frac{1}{2}H_2O$ requires Cl = 12·0 per cent.

An attempt was made to combine benzeneazohydroxyquinoline with ethyl iodide. Under the ordinary pressure no combination occurred, whilst heating in a sealed tube with ethyl alcohol and ethyl iodide at 100° or 120° yielded a brownish-black, crystalline mass of needles, which, on recrystallisation from alcohol, did not melt below 274°. The substance gave only a brown solution in concentrated sulphuric acid instead of the deep magenta of the original:

0·1502 gave 0·2182 CO_2 and 0·0412 H_2O. C = 39·6; H = 3·05.
0·1674 „ 15·5 c.c. N_2 at 22° and 763 mm. N = 10·4.
0·1922 „ 0·1660 AgI. I = 46·7.

The total of the four constituents is 99·7, so that the substance contains practically no oxygen. Treatment with potassium hydroxide failed to remove the iodine, and boiling with zinc and acetic acid effected practically no change in colour. Similar results were obtained with methyl iodide, but in this case a violent outrush of gas resulted on opening the sealed tubes. The substances obtained were not investigated further, but they are obviously not derivatives of hydroxyazoquinoline. The addition of alkyl iodides could not be effected in any of the azo-derivatives of the hydroxyquinoline.

5-p-*Tolueneazo-8-hydroxyquinoline.*

Prepared from *p*-toluenediazonium chloride and an alkaline solution of 8-hydroxyquinoline. The insoluble sodium salt was removed, decomposed with acetic acid, washed and dried. The product crystallised from chloroform in chocolate-brown needles, melting at 174°, and was readily soluble in organic solvents:

0·1702 gave 0·4568 CO_2 and 0·0768 H_2O. C = 73·2; H = 5·0.
0·1440 „ 19·7 c.c. N_2 at 18° and 762 mm. N = 16·1.
$C_{16}H_{13}ON_3$ requires C = 73·0; H = 4·9; N = 16·0 per cent.

Attempts to acetylate or methylate failed, as in the case of benzeneazohydroxyquinoline.

The substance obtained after prolonged heating with acetic anhydride melted at 173°, and gave 16·4 per cent. of nitrogen, agreeing with unchanged tolueneazohydroxyquinoline.

The *hydrochloride*, prepared by heating with concentrated hydrochloric acid, consisted of scarlet needle-shaped crystals; another preparation consisted of almost black plates, but was probably impure:

0·1908 gave 0·0906 AgCl. Cl = 11·7.

$C_{16}H_{13}ON_3,HCl$ requires Cl = 11·85 per cent.

This and all other hydrochlorides are readily hydrolysed. It was found that a solution in concentrated hydrochloric acid, when diluted with water until a concentration of 1·5*N*-acid was reached, gave a precipitate of the base free from halogen.

Dihydrochloride.—0·2946 absorbed 0·0832. HCl = 28·2.

$C_{16}H_{13}ON_3,2HCl$ requires increase = 27·8 per cent.

The salt consists of a violet-black powder.

The *sodium* salt consisted of fine red needles, but, after washing, contained too little sodium for the neutral salt. The *silver* salt yielded too much silver—32·4 per cent., against 29·2 for the neutral silver salt.

The *zinc* salt gave Zn = 8·8 per cent., agreeing with the formula $(C_{16}H_{13}ON_3,HCl)_2ZnCl_2$, and consisted of red needle-shaped crystals.

The *platinichloride*, $(C_{16}H_{13}ON_3)_2,H_2PtCl_6$, contained Pt = 20·6 (calc., Pt = 20·9 per cent.), and was prepared as directed for benzeneazohydroxyquinoline.

5-p-*Bromobenzeneazo*-8-*hydroxyquinoline.*

A solution of *p*-bromobenzenediazonium chloride was poured into an alkaline solution af 8-hydroxyquinoline, and the sodium salt collected, decomposed, and washed as above; it crystallised from chloroform in very small, reddish-brown needles, melting at 215°. The substance dissolves sparingly in alcohol or benzene, but readily in pyridine and other solvents:

0·1508 gave 0·3024 CO_2 and 0·0434 H_2O. C = 54·6; H = 3·25.
0·1614 ,, 17·7 c.c. N_2 at 18° and 762 mm. N = 12·9.
0·3178 ,, 0·1814 AgBr. Br = 24·6.

$C_{15}H_{10}ON_3Br$ requires C = 54·9; H = 3·1; N = 12·8; Br = 24·4 per cent.

The compound cannot be acetylated or methylated. An attempt to combine it with methyl iodide yielded an unworkable tar.

A *monohydrochloride*, consisting of small, bright red plates, melting at 246°, separated from a solution in concentrated hydrochloric acid.

The *dihydrochloride*.—0·1708 absorbed 0·0414 HCl. Increase = 24·2 (calc., increase = 22·3 per cent.). Keeping in moist air resulted in loss of hydrogen chloride, and the final increase in weight was 13·2 per cent.:

$C_{15}H_{10}ON_3Br,HCl,\frac{1}{2}H_2O$ requires increase = 13·8 per cent.

5-p-*Nitrobenzeneazo-8-hydroxyquinoline.*

Prepared from *p*-nitrobenzenediazonium chloride and an alkaline solution of 8-hydroxyquinoline. The alkaline solution of the substance was of a deep blue colour (almost black). It resembles other nitrohydroxyazo-compounds in being sparingly soluble in most organic solvents. It crystallised from pyridine or chloroform in chocolate-coloured, microcrystalline needles, melting at 281°:

0·1522 gave 0·3428 CO_2 and 0·0502 H_2O. C = 51·4; H = 3·7.
0·1488 „ 24·1 c.c. N_2 at 19° and 765 mm. N = 18·9.
$C_{15}H_{10}O_3N_4$ requires C = 61·2; H = 3·4; N = 19·05 per cent.

A *monohydrochloride* was prepared as above, and crystallised in deep red needles, which did not melt below 281°:

0·2768 gave 0·1266 AgCl. Cl = 11·3.
$C_{15}H_{10}O_3N_4,HCl$ requires Cl = 10·7 per cent.

The *sodium* salt is sparingly soluble.

5-p-*Acetylaminobenzeneazo-8-hydroxyquinoline.*

Prepared from *p*-acetylaminobenzenediazonium chloride and an alkaline solution of 8-hydroxyquinoline. The substance is soluble in most organic solvents, but not in benzene or ether. It crystallised from pyridine in deep yellow plates, melting and decomposing at 266°:

0·1512 gave 0·3684 CO_2 and 0·0666 H_2O. C = 66·5; H = 4·9.
0·1414 „ 22·4 c.c. N_2 at 17° and 758 mm. N = 18·5.
$C_{17}H_{14}O_2N_4$ requires C = 66·7; H = 4·6; N = 18·3 per cent.

The compound cannot be acetylated. It yields an orange-yellow *sodium* salt.

5-p-*Aminobenzeneazo-8-hydroxyquinoline.*

Prepared by boiling the foregoing acetyl derivative for two hours with a large excess of 20 per cent hydrochloric acid. The compound was soluble in the usual organic solvents, and crystallised from 50 per cent. aqueous alcohol in dark brown needles, melting and decomposing at 205°. Addition of dilute hydrochloric acid to an alcoholic solution gives a yellow solution; more acid renders the solution red. These changes are probably connected with the formation of mono- and di-hydrochlorides:

0·1622 gave 0·4040 CO_2 and 0·0669 H_2O. C = 68·0; H = 4·6.
0·1202 „ 21·8 c.c. N_2 at 21° and 761 mm. N = 21·5.
$C_{15}H_{12}ON_4$ requires C = 68·2; H = 4·5; N = 21·2 per cent.

The *dihydrochloride*, prepared by evaporation of a solution in concentrated hydrochloric acid, forms chocolate-coloured needles, which do not melt below 281°:

0·2552 gave 0·2188 AgCl. Cl = 21·2.
$C_{15}H_{12}ON_4,2HCl$ requires Cl = 21·0 per cent.

A *trihydrochloride* can be formed by passing hydrogen chloride over the base in a closed vessel; it consists of a dark purple powder:

0·1584 absorbed 0·0672 HCl. Increase = 42·4.
$C_{15}H_{12}ON_4$ requires increase = 41·5 per cent.

The *platinichloride*, prepared in the usual way, consists of a dark brown, microcrystalline powder:

0·2488 gave 0·0726 Pt. Pt = 29·2.
$C_{15}H_{12}ON_4,H_2PtCl_6$ requires Pt = 28·9 per cent.

5-p-*Ethoxybenzeneazo*-8-*hydroxyquinoline*.

Prepared from diazotised *p*-phenetidine hydrochloride and an alkaline solution of 8-hydroxyquinoline. The red *sodium* salt was collected, and treated as above. The azo-compound dissolves in the usual solvents, and crystallises from chloroform in brown needles, having a green reflex, and melting at 176—177°:

0·1502 gave 0·3812 CO_2 and 0·0694 H_2O. C = 69·3; H = 5·1.
0·1290 „ 16·0 c.c. N_2 at 22° and 764 mm. N = 14·7.
$C_{17}H_{15}O_2N_3$ requires C = 69·6; H = 5·1; N = 14·3 per cent.

The *hydrochloride*, prepared by evaporation with concentrated hydrochloric acid, separates in chocolate-brown needles, melting at 227°:

0·1888 gave 0·0884 AgCl. Cl = 11·6.
$C_{17}H_{15}O_2N_3,HCl$ requires Cl = 11·9 per cent.

Hydrogen chloride passed over the base gave the following results:

0·1562 gained 0·0548 HCl. Increase = 35·1.
$C_{17}H_{15}O_2N_3,2HCl$ requires increase = 24·9 per cent.
$C_{17}H_{15}O_2N_3,3HCl$ „ increase = 37·4 „

The substance therefore tends to form a trihydrochloride.

In order to ascertain whether the azo-compounds of this class were para-hydroxy-compounds, the dye was reduced by tin and hydrochloric acid, and the tin removed by hydrogen sulphide; the solution was evaporated to small bulk with hydrochloric acid, filtered from some tarry matter, neutralised with sodium carbonate, and rendered slightly acid with sulphuric acid. After some hours the characteristic tufts of colourless, silky needles of 5-amino-8-hydroxyquinoline sulphate described by Fischer and Renouf (*Ber.*, 1884, **17**, 1642) separated.

5-α-*Naphthaleneazo-8-hydroxyquinoline.*

A solution of α-naphthalenediazonium chloride was poured into an alkaline solution of 8-hydroxyquinoline. The reddish-brown *sodium* salt was decomposed with acetic acid, and the product washed and dried. The material was best purified by repeated boiling with alcohol, the residue being found to be pure. With some difficulty, microcrystalline, chocolate-coloured needles, melting at 252—253°, were obtained from benzene. The compound dissolves sparingly in organic solvents. It is noteworthy that the solution of the substance in concentrated sulphuric acid is deep blue:

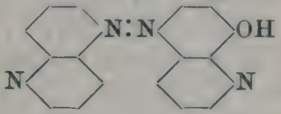
0·1042 gave 0·2922 CO_2 and 0·0378 H_2O. C = 76·5; H = 4·0.
0·1688 ,, 20·5 c.c. N_2 at 19° and 762 mm. N = 14·15.
$C_{19}H_{13}ON_3$ requires C = 76·25; H = 4·35; N = 14·0 per cent.

This substance cannot be acetylated.

The *hydrochloride*, prepared by evaporation with hydrochloric acid, occurs in reddish-brown, microcrystalline needles:

0·1828 gave 0·0802 AgCl. Cl = 10·85.
$C_{19}H_{13}ON_3,HCl$ requires Cl = 10·6 per cent.

Quinolineazo-8-hydroxyquinoline,



10·8 Grams of 5-aminoquinoline dihydrochloride were diazotised and poured into an alkaline solution of 7·2 grams of 8-hydroxyquinoline. The red *sodium* salt was decomposed with acetic acid, the product washed, dried, and boiled several times with alcohol. The compound is slightly soluble in benzene and insoluble in ether, but dissolves to a somewhat greater extent in other solvents. It separates from a solution in chloroform as an amorphous, dirty-brown powder, melting and decomposing at 268°. The solution in alcohol is reddish-yellow; a drop of dilute hydrochloric acid produces a bright yellow solution, and further addition of acid changes the colour to a deep orange shade. No acetyl compound could be obtained. Heating under pressure with methyl iodide yielded a tarry mass and gaseous products. Prolonged boiling under the ordinary pressure with methyl alcohol and methyl iodide resulted in the formation of a small quantity of material containing halogen, but the amount was too small for further examination:

0·1432 gave 0·3802 CO_2 and 0·0536 H_2O. C = 72·4; H = 4·2.
0·1328 ,, 21·8 c.c. N_2 at 20° and 760 mm. N = 19·0.
$C_{18}H_{12}ON_4$ requires C = 72·0; H = 4·0; N = 18·7 per cent.

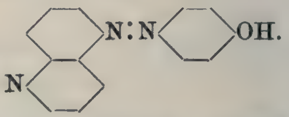
The *dihydrochloride*, prepared by evaporation with concentrated hydrochloric acid, consists of magenta-coloured needles, which do not melt below 281°:

0·2386 gave 0·1876 AgCl. Cl = 19·4.
$C_{18}H_{12}ON_4,2HCl$ requires Cl = 19·0 per cent.

Trihydrochloride.—0·1742 absorbed 0·0678 HCl. Increase = 39·0.
$C_{18}H_{12}ON_4$ requires increase = 36·5 per cent.

This substance was a purple-black powder.

Quinolineazophenol,



Prepared from diazotised 5-aminoquinoline and an alkaline solution of phenol. A deep magenta-coloured solution resulted, but no salt deposited. The liquid was acidified with acetic acid; the brownish-yellow precipitate formed was collected, washed with water and a little hot alcohol. It crystallised from alcohol in light brown, microcrystalline needles, melting at 274°. The compound dissolves in ordinary organic solvents, but is difficult to obtain in crystals of fair size, resembling hydroxyazobenzene in this respect:

0·1366 gave 0·3602 CO_2 and 0·0600 H_2O. C = 71·9; H = 4·9.
0·1444 ,, 21·1 c.c. N_2 at 22° and 764 mm. N = 17·2.
$C_{15}H_{11}ON_3$ requires C = 72·3; H = 4·4; N = 16·9 per cent.

The substance is readily acetylated by boiling for a few hours with an equal weight of anhydrous sodium acetate and 15 parts of acetic anhydride. The acetate separates from 50 per cent. alcohol in slender, light brown plates, melting at 192—193°.

As the crystallised material retained water, it was dried at 100° before analysis:

0·1108 gave 0·2832 CO_2 and 0·0472 H_2O. C = 69·7; H = 4·7.
0·1236 ,, 15·6 c.c. N_2 at 19° and 759 mm. N = 14·65.
$C_{17}H_{13}O_2N_3$ requires C = 70·1; H = 4·5; N = 14·4 per cent.

Quinolineazophenyl acetate is insoluble in cold sodium hydroxide solution, but gradually dissolves on warming, giving the magenta-coloured solution of quinolineazophenol.

Quinolineazophenol reacts with sodium ethoxide and ethyl iodide in boiling alcoholic solution, and yields the ethyl ether, but a small proportion of the substance reacts with ethyl iodide directly to form an ethiodide. The alcoholic solution of the ethyl ether was diluted with much water, and the brown precipitate collected, washed with water, and dried on a porous tile. The dried mass was extracted with hot alcohol, leaving an almost black ethiodide, which was tarry, and was not further examined. The alcoholic extract was diluted with an equal quantity of water, boiled, filtered, and allowed to crystallise. Long, light brown needles, melting at 126°, separated, the crystals giving a faint test for halogens:

0·1384 gave 18·9 c.c. N_2 at 21° and 752 mm. N = 15·6.

$C_{17}H_{15}ON_3$ requires N = 15·2 per cent.

Quinolineazophenetole dissolves in alcohol with a yellow colour; it is insoluble in sodium hydroxide solution, but with dilute or concentrated acids produces similar colour changes to the parent substance. This compound, like the acetate, retains a little water, which can only be driven off by prolonged drying at 100°.

Quinolineazophenol hydrochloride was prepared by evaporation with concentrated hydrochloric acid; it does not melt below 281°:

0·1882 gave 0·0932 AgCl. Cl = 12·2.

$C_{15}H_{11}ON_3,HCl$ requires Cl = 12·4 per cent.

The *dihydrochloride* was prepared by passing hydrogen chloride over the powdered material moistened with a little chloroform; it consists of a dark red powder:

0·1902 gained 0·0565 HCl. Increase = 29·8.

$C_{15}H_{11}ON_3$ requires increase = 29·3 per cent.

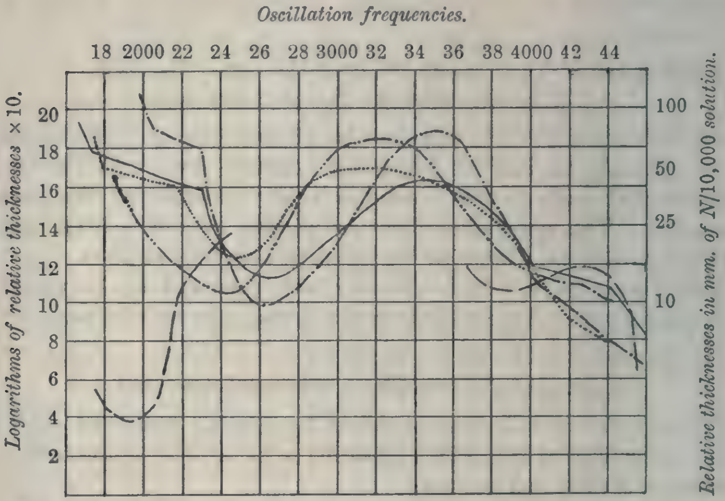
This salt loses its hydrogen chloride very slowly as compared with the dihydrochloride of benzeneazohydroxyquinoline, two or three days' exposure to moist air resulting in the same loss as occurs with the latter compound in half an hour, namely, one molecule of hydrogen chloride.

Ethoxyquinolineazophenol.

For this preparation, 8-ethoxy-5-aminoquinoline was required, and was prepared by Vis's method (*J. pr. Chem.*, 1892, [ii], **45**, 530). The diazotisation was troublesome, as frothing occurred to a slight extent, but by rapid diazotisation and filtration into the alkaline solution of phenol a deep magenta solution resulted, which, on acidification with acetic acid, gave a yellowish-brown precipitate, which was washed and dried. Repeated crystallisation from alcohol furnished light brown, microcrystalline prisms, melting at 256°, and soluble in organic solvents other than benzene and ether:

0·1306 gave 0·3324 CO_2 and 0·0612 H_2O. C=69·4; H=5·2.
0·1128 ,, 14·1 c.c. N_2 at 21° and 760 mm. N=14·4.
$C_{17}H_{15}O_2N_3$ requires C=69·6; H=5·1; N=14·3 per cent.

Sufficient of the substance was not available to prepare any quantity of the acetate, but when acetylated in the usual way a sandy powder resulted, which crystallised from alcohol in minute plates, melting at 183°, and did not dissolve in cold sodium hydroxide, but gave a deep magenta solution after heating for a few minutes.



Full curve:	5-*Benzeneazo*-8-*hydroxyquinoline in alcohol.*
Dash curve:	5-*Benzeneazo*-8-*hydroxyquinoline in concentrated hydrochloric acid.*
Dot and dash curve:	*Quinolineazophenol in alcohol.*
Dotted curve:	*Quinolineazo*-8-*hydroxyquinoline in alcohol.*
2 Dots and dash curve:	5-p-*Aminobenzeneazo*-8-*hydroxyquinoline in alcohol.*

The changes in the colour of the solutions of the foregoing compounds under the action of strong mineral acids due to the formation of oxonium salts is strikingly shown by all these substances. In alcoholic solution all of them, on the addition of a little dilute hydrochloric acid, produce a yellow or, at most, an orange-coloured solution. Concentrated hydrochloric acid gives colours varying from deep red with *p*-nitrobenzeneazohydroxyquinoline to deep violet in the case of benzeneazohydroxyquinoline. Concentrated sulphuric acid gives varying shades of magenta and purple, but with *α*-naphthaleneazohydroxyquinoline a deep blue solution was obtained. Sodium hydroxide added to the alcoholic solutions produces reddish-yellow or red solutions, except with *p*-nitrobenzeneazohydroxyquinoline, which becomes violet. This behaviour towards concentrated acids, with the resulting formation of oxonium salts is entirely in accord with the supposition "that a decrease in the principal vibration frequency of an azo-compound accompanies an increase in the length of chain of conjugated double linkings" (Hewitt and Mitchell, Trans., 1907, **91**, 1251; Hewitt and Thole, Trans., 1909, **53**, 1395). The curves of the absorption spectra (see figure) are of particular interest, inasmuch as they show that the heads of the bands are in practically the same position as was observed by Hewitt and Thomas (Trans., 1909, **95**, 1297) in the case of aminobenzeneazophenol and dimethylaminobenzeneazophenol, and are such as are given by hydroxyazo-compounds. The solution of the dihydrochloride of benzeneazohydroxyquinoline in concentrated hydrochloric acid could not be examined in greater thickness than those shown because of the intense colour; hence it was not possible to furnish a complete curve, but the two branches shown are obviously part of one curve. Benzeneazohydroxyquinoline and quinolineazophenol give curves which differ only in the somewhat greater persistency of the band in the latter; whilst the band of quinolineazohydroxyquinoline is least persistent of all, but does not differ from the other curves to such an extent as to indicate an alteration in the configuration of the molecule.

It has been found troublesome to diazotise 8-aminoquinoline satisfactorily, so that rather poor yields of the hydroxyazo-derivatives of this substance have been obtained, but these can be acetylated fairly readily, and the work is still proceeding. As regards the azo-derivatives of 8-hydroxyquinoline, no attempt to acetylate by other than the usual methods was made, it being considered sufficient for comparison with the quinolineazophenols to attempt the acetylation by the ordinary methods.

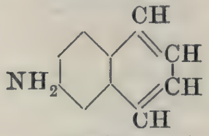
EAST LONDON COLLEGE.

CXXIII.—*The Colour and Constitution of the Aminocoumarins.*

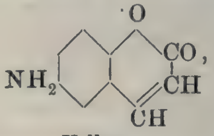
By Arthur Clayton, B.Sc., A.R.C.S.

The introduction of an amino-group into the molecule of a colourless substance does not generally cause the production of colour, but a peculiar exception is met with in the case of 6-aminocoumarin, which possesses a deep yellow colour, although coumarin itself is colourless. The cause of the yellow colour was investigated by Morgan and Micklethwait (Trans., 1904, **85**, 1230), who showed that the colour was not affected by the substitution of methyl for one or both aminic hydrogen atoms, but was destroyed by acylation or by the formation of a quaternary salt. These investigators concluded that the cause of the colour lies in some relation between the aminic nitrogen atom and the unsaturated ·O·CO· group present in the lactonic ring, this conclusion being supported by the amino-group occupying a para-position with respect to the lactonic oxygen. The author of the present communication has examined a number of amino-derivatives of coumarin and its homologues with the view of obtaining further insight into the cause of the yellow colour.

Since β-naphthylamine is colourless and the only difference between the formulæ of this substance and 6-aminocoumarin is the substitution of the ·O·CO· group in the latter compound for the ·CH:CH· group present in the former (see formulæ), it follows that the group ·O·CO· is directly involved in the production of the colour. Similarly, the amino-group is involved, because coumarin is colourless. It has been shown by Morgan and Micklethwait (*loc. cit.*) that a mobile hydrogen atom in the amino-group does not give rise to the colour, as 6-dimethylaminocoumarin is yellow. The remaining factors possibly involved are:



Colourless.



Yellow.

1. The position in the benzenoid ring occupied by the amino-group.
2. The presence of a mobile hydrogen atom in the benzenoid ring.
3. The presence of a mobile hydrogen atom in the lactonic ring.
4. A direct connection between the ·O·CO· and amino-groups, depending on or independent of their relative positions.

(1) 5-*Amino*-6: 7-*dimethylcoumarin*, 6-*amino*-7-*methylcoumarin*,

*7-amino-*5 : 6 : 8*-trimethylcoumarin*, 8*-aminocoumarin*, and 5 : 8*-diamino-*6 : 7*-dimethylcoumarin* were prepared by reducing the corresponding colourless nitro-compounds, and were in each case found to be yellow. As the above compounds contain the amino-group in each possible position in the benzenoid ring, the production of colour does not depend on the position occupied by the amino-group.

(2) Since 7-amino-5 : 6 : 8-trimethylcoumarin is yellow, and in this compound the benzenoid ring is completely substituted, the presence of a mobile hydrogen atom in the benzenoid ring is not involved in the colour formation.

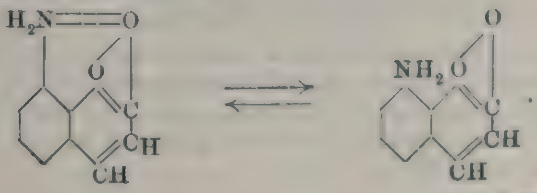
(3) 6*-Amino-*4 : 7*-dimethylcoumarin*, 5*-amino-*4 : 6 : 7*-trimethylcoumarin*, 5 : 7*-diamino-*4 : 6 : 8*-trimethylcoumarin*, and 6*-amino-*3 : 4 : 7*-trimethylcoumarin* were prepared, and all found to be yellow, hence the presence of a mobile hydrogen atom in the lactonic ring is not necessary for the production of the colour.

(4) The formation of the yellow colour appears from the above observations to be consequent on some direct connexion between the ·O·CO· and amino-groups, and the results obtained in (1) show this connexion to be independent of the relative position of these groups.

Coumarin and its derivatives exhibit additive properties due to the unsaturation of the ·O·CO· group (Williamson, *Journ. Chem. Soc.*, 1875, **28**, 850; Morgan and Micklethwait, Trans., 1906, **89**, 863; Clayton, Trans., 1908, **93**, 524), which possesses an amphoteric nature. There is, however, a much greater tendency to combine with basic substances than with acids, so the residual affinities of the ·O·CO· group may be considered to be of a weakly acid nature.

In the case of the aminocoumarins, these acid affinities would doubtless find partial satisfaction in the extra affinities available in the aminic nitrogen atom, but owing to the weakness of the union which would exist between the ·O·CO· and amino-groups, it is highly probable that the bonds uniting them would be continually broken and re-formed during intermolecular motions.

If the correct formula for coumarin is that suggested by Morgan and Micklethwait (Trans., 1906, **89**, 863), the amino-coumarins may be undergoing the vibratory change indicated in the subjoined formulæ for 8-aminocoumarin:



The author considers it possible that these vibrations may generate the yellow colour, and it is worthy of note that in the case of 8-aminocoumarin, where, owing to the proximity of the nitrogen and oxygen atoms concerned, the rupture of the bonds would be less easily effected, the yellow colour is much less marked than in the other amino-derivatives.

The following facts support the view expressed by the above formulæ:

(i) The above observation (p. 1350), that the colour vanishes when the supplementary valencies of the nitrogen atom are involved by the formation of a quaternary salt, and when the basicity of the amino-group is destroyed by acylation.

(ii) The fact that the hydrochlorides of all the amino-coumarins examined by the author are colourless.

(iii) The remarkable stability of the amino- and diamino-coumarins both in the solid state and in solution.

EXPERIMENTAL.

8-*Aminocoumarin.*—8-Nitrocoumarin (1 gram) was suspended in boiling dilute acetic acid (100 c.c.), and gradually treated with iron filings (1 gram), after which the mixture was boiled for fifteen minutes, and filtered. The filtrate yielded crystals, which, after recrystallisation from alcohol, formed pale yellow prisms, melting at 145—146°:

0·1987 gave 0·4868 CO_2 and 0·0817 H_2O. C = 66·81; H = 4·57.
0·1023 ,, 7·5 c.c. N_2 at 20° and 756 mm. N = 8·34.
$C_9H_7O_2N$ requires C = 67·08; H = 4·35; N = 8·70 per cent.

6-*Amino-7-methylcoumarin.*—A mixture of 6-nitro-7-methylcoumarin (1 gram) and 5 per cent. acetic acid (100 c.c.) was heated to boiling and gradually treated with iron filings (1 gram), after which the liquid was boiled for fifteen minutes, then cooled and filtered. The residue was extracted with alcohol and crystallised from the same solvent, when yellow needles, melting at 200—201°, were obtained:

0·1523 gave 0·3818 CO_2 and 0·0729 H_2O. C = 68·37; H = 5·32.
0·1216 ,, 8·7 c.c. N_2 at 20° and 756 mm. N = 8·14.
$C_{10}H_9O_2N$ requires C = 68·57; H = 5·14; N = 8·00 per cent.

6-*Amino-4:7-dimethylcoumarin* was prepared from 6-nitro-4:7-dimethylcoumarin in the manner described in the preceding experiment. The product, however, was extracted with glacial acetic acid, and crystallised from this solvent in yellow needles, melting at 203—205°:

0·1781 gave 0·4540 CO_2 and 0·0941 H_2O. C = 69·52; H = 5·87.
0·1816 „ 12·0 c.c. N_2 at 20° and 756 mm. N = 7·52.
$C_{11}H_{11}O_2N$ requires C = 69·84; H = 5·82; N = 7·41 per cent.

5-*Amino*-6 : 7-*dimethylcoumarin*.—5-Nitro-6 : 7-dimethylcoumarin (1 gram) and dilute acetic acid (80 c.c.) were boiled together, and gradually treated with iron filings (0·8 gram), after which the mixture was heated for one hour. The cooled liquid was filtered and the residue extracted with alcohol, from which solvent yellow needles, melting at 189°, were obtained:

0·1630 gave 0·4148 CO_2 and 0·0871 H_2O. C = 69·38; H = 5·94.
0·1590 „ 10·7 c.c. N_2 at 21° and 752 mm. N = 7·54.
$C_{11}H_{11}O_2N$ requires C = 69·84; H = 5·82; N = 7·41 per cent.

7-*Amino*-5 : 6 : 8-*trimethylcoumarin*. — 7-Nitro-5 : 6 : 8-trimethylcoumarin (5 grams) was mixed with dilute acetic acid (100 c.c.) and heated to boiling, when iron filings (5 grams) were gradually added, the mixture finally being boiled for one hour. The cooled liquid was filtered, and the residue repeatedly extracted with alcohol, in which solvent the product is somewhat sparingly soluble. Recrystallisation from glacial acetic acid yielded yellow needles, melting at 220—221°. The solution in alcohol or acetone exhibits a strong blue fluorescence, which does not appear in the solutions in benzene, toluene, or acetic acid:

0·1331 gave 0·3458 CO_2 and 0·0782 H_2O. C = 70·86; H = 6·60.
0·1341 „ 7·9 c.c. N_2 at 20° and 756 mm. N = 6·70.
$C_{12}H_{13}O_2N$ requires C = 70·94; H = 6·40; N = 6·90 per cent.

6-*Amino*-4 : 6 : 7-*trimethylcoumarin*. — 6-Nitro-4 : 6 : 7-trimethylcoumarin (2 grams) and dilute acetic acid (40 c.c.) were boiled together and treated with iron filings (2 grams), after which the mixture was boiled for one hour. The cooled liquid was filtered and the residue extracted with alcohol, from which solvent 75 per cent. of the theoretical quantity of yellow needles, melting at 232—233°, was obtained. The substance is rather sparingly soluble in alcohol:

0·1812 gave 0·4699 CO_2 and 0·1047 H_2O. C = 70·71; H = 6·42.
0·1851 „ 11·3 c.c. N_2 at 20° and 750 mm. N = 6·89.
$C_{12}H_{13}O_2N$ requires C = 70·94; H = 6·40; N = 6·90 per cent.

6-*Nitro*-3 : 4 : 7-*trimethylcoumarin*.—A solution of 3 : 4 : 7-trimethylcoumarin (2·3 grams) in concentrated sulphuric acid (12 c.c.) was slowly treated at 0° with a mixture of nitric acid (D 1·4) (1 c.c.) and concentrated sulphuric acid (3 c.c.), after which the liquid was kept at the ordinary temperature for thirty minutes, and then poured on crushed ice. The product crystallised from glacial acetic acid in colourless needles, melting at 169—170°:

0·1994 gave 0·4515 CO_2 and 0·0832 H_2O. C = 61·76; H = 4·64.
0·1514 „ 7·9 c.c. N_2 at 20° and 756 mm. N = 5·93.
$C_{12}H_{11}O_4N$ requires C = 61·80; H = 4·72; N = 6·01 per cent.

6-*Amino*-3 : 4 : 7-*trimethylcoumarin.* — 6-Nitro-3 : 4 : 7-trimethylcoumarin was reduced with iron filings and dilute acetic acid in the usual way, the liquid being boiled for twenty minutes after the addition of the iron. The cooled mixture was filtered, and the residue extracted with alcohol, from which solvent the product crystallised in yellow needles, melting at 200—201°. The alcoholic solution exhibits a brilliant green fluorescence:

0·1450 gave 0·3759 CO_2 and 0·0820 H_2O. C = 70·70; H = 6·28.
0·1047 „ 6·7 c.c. N_2 at 20° and 756 mm. N = 7·32.
$C_{12}H_{13}O_2N$ requires C = 70·94; H = 6·40; N = 6·90 per cent.

5 : 8-*Diamino*-6 : 7-*dimethylcoumarin.* — 5 : 8-Dinitro-6 : 7-dimethylcoumarin (2 grams) was heated to 100° with dilute acetic acid and gradually treated with iron filings (5 grams), the mixture being subsequently boiled for twenty minutes, then cooled and filtered. The residue was extracted with alcohol, from which solvent yellow needles, melting at 209—212°, were obtained:

0·1330 gave 16·0 c.c. N_2 at 20° and 762 mm. N = 13·79.
$C_{11}H_{12}O_2N_2$ requires N = 13·73 per cent.

5 : 7-*Diamino*-4 : 6 : 8-*trimethylcoumarin.* — 5 : 7-Dinitro-4 : 6 : 8-trimethylcoumarin was reduced with iron filings and acetic acid as in the preceding experiment. The product separated from alcohol in fine, yellow needles, melting at 218—220°. There was no tendency in this or the preceding experiment to form the nitro-amine:

0·1403 gave 0·3381 CO_2 and 0·0781 H_2O. C = 65·72; H = 6·18.
0·1093 „ 12·3 c.c. N_2 at 18° and 734 mm. N = 12·55.
$C_{12}H_{14}O_2N_2$ requires C = 66·05; H = 6·42; N = 12·84 per cent.

The author desires to express his thanks to the Chemical Society for a grant which has in part defrayed the expense incurred during this investigation.

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CXXIV.—*Experiments on the Walden Inversion. Part V. The Interconversion of the Optically Active α-Hydroxy-β-phenylpropionic Acids.*

By Alex. McKenzie and Henry Wren.

The β-hydroxy-β-phenylpropionic acids (this vol., p. 121) and the isomeric phenylmethylglycollic acids (this vol., p. 1016) have already been investigated with reference to the Walden inversion.

In the present communication the resolution of another of the isomeric racemic "phenyl-lactic" acids, namely, α-hydroxy-β-phenylpropionic acid, $C_6H_5{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H$, into its optically active components is described. An aqueous solution of this acid was neutralised by morphine, and the resolution proceeded with the same ease as in the case of the β-hydroxy-acid (*loc. cit.*), the morphine *d*-salt being much more sparingly soluble in water than the morphine *l*-salt. The resulting *d*-acid melts at 124—125°, whereas the *r*-acid melts at 97—98°. The value for the specific rotation, $[\alpha]_D + 18{\cdot}5°$ for $c = 3{\cdot}5332$ in ethyl-alcoholic solution, is nearly identical with that obtained for the β-hydroxy-acid under similar conditions. The *l*-acid was readily isolated from the filtrate, from which the morphine *d*-salt had separated.

The preparation of the optically active α-bromo-β-phenylpropionic acids from the inactive bromo-acid has been described by E. Fischer and Carl (*Ber.*, 1906, **39**, 3996). We find that the displacement of bromine by the hydroxy-group in these acids takes place very much more slowly than in any other case of halogen displacement described in this series of papers, and it is not accompanied by a change of sign of rotation. Since it is immaterial whether the displacement is effected by water, by aqueous sodium hydroxide, or by silver oxide and water, the action

$$l\text{-}C_6H_5{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2H \longrightarrow l\text{-}C_6H_5{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H,$$

appears to be a normal one.

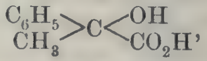
The action of phosphorus pentachloride on the active hydroxy-acids was next examined. The *d*-acid gave a dextrorotatory chloro-acid chloride, the phosphorus pentachloride, as is always the case when it acts on an optically active acid, causing a considerable amount of racemisation. When the acid chloride was heated with calcium carbonate and water, a change of sign was found to have occurred; a lævorotatory product was obtained, from which a specimen of the pure *l*-hydroxy-acid was isolated. The behaviour of the *l*-hydroxy-acid towards phosphorus pentachloride was similar. The following changes have been carried out:

$$\begin{tikzcd}
d\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H \arrow[r, "\text{(by } PCl_5\text{)}"] & l\text{-}C_6H_5\cdot CH_2\cdot CHCl\cdot CO_2H \arrow[d, "\text{(by } CaCO_3 \text{ and water)}"] \\
d\text{-}C_6H_5\cdot CH_2\cdot CHCl\cdot CO_2H \arrow[u, "\text{(by } CaCO_3 \text{ and water)}"] & l\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H. \arrow[l, "\text{(by } PCl_5\text{)}"]
\end{tikzcd}$$

This is the first example recorded where phosphorus pentachloride appears to act abnormally.

The isomeric acids,

$C_6H_5\cdot CH(OH)\cdot CH_2\cdot CO_2H$, $C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H$, and



$$\begin{matrix}C_6H_5\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\CO_2H\end{matrix},$$

thus differ from one another in behaviour from the point of view of the Walden inversion.

Since phosphorus pentachloride has been found to be an agent capable of causing a transformation such as the above, and since the action of thionyl chloride on the active phenylmethylglycollic acids also proceeded in a somewhat unexpected manner (*loc. cit.*), the comparison of the action of these two chlorides on a number of active hydroxy-acids and their esters has been rendered necessary. This subject is at present under investigation.

EXPERIMENTAL.

Resolution of r-*α-Hydroxy-β-phenylpropionic Acid.*

r-*α*-Hydroxy-*β*-phenylpropionic acid was prepared from benzylbromomalonic acid (Conrad, *Annalen*, 1880, **204**, 174) by converting it into *α*-bromo-*β*-phenylpropionic (*α*-bromohydrocinnamic) acid, and then displacing the bromine in the latter acid by the hydroxy-group (E. Fischer, *Ber.*, 1904, **37**, 3062; E. Fischer and Carl, *loc. cit.*; E. Fischer and Zemplén, *Ber.*, 1909, **42**, 4878).

14·7 Grams of the *r*-acid (1 mol.) were dissolved in 300 c.c. of water at about 90°, and shaken with 26·5 grams of powdered morphine (1 mol.) for a few minutes until the alkaloid had dissolved. After a night at about 8°, 24 grams of glassy crystals had separated. After crystallisation from water, 18 grams of salt were obtained, from which the acid was isolated by acidification with mineral acid and extraction with ether. The resulting acid was crystallised once from water (50 c.c.), and 4·2 grams of the pure *d*-acid were obtained.

d-*α-Hydroxy-β-phenylpropionic acid*, $C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H$, dissolves readily in cold methyl alcohol, ethyl alcohol, or acetone. It is readily soluble in hot water or benzene, and, on cooling, separates in long, glassy needles, with rectangular ends. It melts at 124—125°:

0·1507 gave 0·3578 CO_2 and 0·0829 H_2O. C = 64·8; H = 6·2.

$C_9H_{10}O_3$ requires C = 65·0; H = 6·1 per cent.

Its rotation was determined in ethyl-alcoholic solution:

$$l = 4,\ c = 3{\cdot}5332,\ \alpha_D^{12}\ +2{\cdot}61^\circ,\ [\alpha]_D^{12}\ +18{\cdot}5^\circ.$$

Its melting point and its specific rotation in ethyl-alcoholic solution did not change after it had been recrystallised several times from water.

Its rotation was also determined in aqueous solution:

$$l = 4,\ c = 2{\cdot}5622,\ \alpha_D^{13\cdot5}\ +2{\cdot}34^\circ,\ [\alpha]_D^{13\cdot5}\ +22{\cdot}8^\circ.$$

The enantiomorphously related acid was obtained from the mother liquors, from which the morphine *d*-salt had separated. The crude acid (7·5 grams) was crystallised from water (70 c.c.); the yield of the *l*-acid was 4 grams. It was obvious that the difference in solubility in water between the active and the inactive isomerides was such as to render the isolation of the pure active acid from a mixture of active and inactive acids a simple operation in the case mentioned.

l-*α-Hydroxy-β-phenylpropionic acid*, like the *d*-acid, melts at 124—125°:

0·1309 gave 0·3124 CO_2 and 0·0716 H_2O. C = 65·1; H = 6·1.

$C_9H_{10}O_3$ requires C = 65·0; H = 6·1 per cent.

A determination of its specific rotation in ethyl-alcoholic solution gave the result:

$$l = 4,\ c = 2{\cdot}9332,\ \alpha_D^{12}\ -2{\cdot}19^\circ,\ [\alpha]_D^{12}\ -18{\cdot}7^\circ.$$

In another experiment, where 18 grams of the *r*-acid, 410 c.c. of water, and 33 grams of morphine were employed, crystallisation was induced by the addition of a nucleus of the morphine *d*-salt. From the 22·5 grams of salt which separated after a night at about 9°, 6·1 grams of nearly pure *d*-acid were obtained, with $[\alpha]_D\ +17{\cdot}8^\circ$ for $c = 6{\cdot}748$ in ethyl-alcoholic solution. After one crystallisation from water, the acid was obtained with the rotation quoted above. The filtrate, from which the morphine *d*-salt had been removed, gave 6·1 grams of acid, which had $[\alpha]_D\ -16{\cdot}8^\circ$ for $c = 6{\cdot}95$ in ethyl-alcoholic solution, and, after one crystallisation from water, the acid was pure.

The resolution of the inactive acid is accordingly very easily carried out; possibly the addition of a nucleus of the morphine *d*-salt is of service.

Displacement of Bromine in the Active α-Bromo-β-phenylpropionic Acids by the Hydroxy-group.

Fischer and Carl (*loc. cit.*) employed both brucine and quinine for the resolution of inactive α-bromo-β-phenylpropionic acid. The most active product obtained by them had $[\alpha]_D$ −8·3°, but, since it was frozen out from a mixture of *r*- and *l*-acids at 0°, it contained, as Fischer and Carl point out, some of the *r*-form. The various specimens of acids used in the following experiments were prepared by the quinine method, and were also not homogeneous.

Action of Water.—The bromo-acid used had $[\alpha]_D$ −5·1° in ethyl-alcoholic solution. A solution of 2·5 grams in 200 c.c. of water was heated at 100° for about fifty hours, but, even after this treatment, the displacement of the bromine by the hydroxy-group was not complete. The resulting acid was crystallised once from benzene, in which the bromo-acid is readily soluble; the hydroxy-acid obtained was lævorotatory, having $[\alpha]_D$ −5·6° in ethyl-alcoholic solution.

Similarly, a dextrorotatory bromo-acid, with $[\alpha]_D$ +7·4° in ethyl-alcoholic solution, was heated with water in an open dish for about thirty hours, the water being renewed from time to time. The hydroxy-acid, obtained as before, had $[\alpha]_D$ +12·7° in ethyl-alcoholic solution.

Action of Calcium Carbonate and Water.—The dextrorotatory bromo-acid, as used in the preceding experiment, was boiled for several hours with water and calcium carbonate. The resulting hydroxy-acid, after one crystallisation from water, was free from bromine, and had $[\alpha]_D$ +15·8° in ethyl-alcoholic solution.

Action of Aqueous Sodium Hydroxide.—A solution of 1·1 grams of bromo-acid, with $[\alpha]_D$ +7·4° in 110 c.c. of aqueous sodium hydroxide (0·1047*N*), was heated for four hours at about 100°. The resulting acid was crystallised from benzene, and the practically pure *d*-hydroxy-acid obtained.

Action of Mercuric Oxide and Water.—Here again a dextrorotatory bromo-acid gave the *d*-hydroxy-acid.

Action of Water on Silver d-*α-Bromo-β-phenylpropionate.*—The dextrorotatory bromo-acid, with $[\alpha]_D$ +5·2° in ethyl-alcoholic solution, was converted into silver salt, which was heated with an excess of water for nine hours at 100°. The resulting acid, after one crystallisation from benzene, had $[\alpha]_D$ +13·4° in ethyl-alcoholic solution.

When the dextrorotatory bromo-acid was heated with silver oxide and water at 100°, partial oxidation took place, but the resulting hydroxy-acid was dextrorotatory.

Interconversion of the Optically Active Hydroxy-acids.

d-α-Hydroxy-β-phenylpropionic acid (5·7 grams) was mixed with phosphorus pentachloride (14 grams). The evolution of hydrogen chloride began at the ordinary temperature. The mixture was connected with a tube condenser, and gradually heated to 140° during an interval of three hours. After one hour at 140—145°, the action was not quite complete. The phosphoryl chloride was accordingly distilled off, and the temperature maintained at 195—205° during two hours. No phosphorus pentachloride separated on cooling. The product was distilled under diminished pressure, and an oil, boiling mainly at 115—117°/9 mm., was collected. This was diluted slightly with ether, and examined polarimetrically in a 50 mm. tube; it had α_D +4·0°. The oil was then boiled with a large excess of calcium carbonate and water for eight hours. The acid was extracted and found to be *laevorotatory*, giving the value $[\alpha]_D$ −11·9° in ethyl-alcoholic solution. After one crystallisation from benzene, the product melted at 123—125°, and had $[\alpha]_D$ −16·3° in ethyl-alcoholic solution. It was then crystallised from water. The resulting acid melted at 124—125°, and had $[\alpha]_D$ −18·0° in ethyl-alcoholic solution.

The identity of this acid with the pure *l*-hydroxy-acid was further shown by a determination of the melting point of a mixture of the two.

The *l*-hydroxy-acid was converted into the *d*-hydroxy-acid in a similar manner.

A further experiment was carried out with the *d*-hydroxy-acid under conditions somewhat different from the above. The acid (5·2 grams) was heated with phosphorus pentachloride (19·6 grams), the latter being taken in this case in excess. The temperature was gradually raised to 150° during two hours, the phosphoryl chloride then distilled off, and the temperature gradually raised to 190° during thirty minutes. The product was then added to ice and treated with calcium carbonate and water as before. After removal of the excess of calcium carbonate, the filtrate (75 c.c.) was lævorotatory, 25 c.c. of it in a 4-dcm. tube giving α_D −1·09°. The acid extracted from the calcium salt had $[\alpha]_D$ −9·6° in ethyl-alcoholic solution.

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CXXV.—*The Triazo-group. Part XIV. Azoimides of the Acetoacetic Series.*

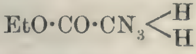
By MARTIN ONSLOW FORSTER and SIDNEY HERBERT NEWMAN.

As a natural sequence to the series of substituted triazomalonic esters (this vol., p. 126), we proceeded to study the corresponding derivatives of acetoacetic ester, and it may be stated at once that the result has been somewhat disappointing, on account of the subsidiary changes which take place under the conditions usually observed for the displacement of halogen by the triazo-group. For this reason it has not been possible to produce α- or γ-triazoacetoacetic ester, and although a small quantity of αα-bistriazoacetoacetic ester has been isolated, the yield of this material, owing to circumstances which are explained later, is scarcely more than 5 per cent. By the interaction of methyl and ethyl α-chloromethylacetoacetates, and of ethyl α-chloroethylacetoacetate with sodium azide, however, the corresponding triazo-derivatives,

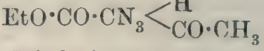
$$CH_3\cdot CO\cdot CN_3(CH_3)\cdot CO_2\cdot CH_3, \quad CH_3\cdot CO\cdot CN_3(CH_3)\cdot CO_2\cdot C_2H_5, \text{ and } CH_3\cdot CO\cdot CN_3(C_2H_5)\cdot CO_2\cdot C_2H_5,$$

have been prepared, but it has to be noted that substitution of the azoimide nucleus for chlorine in this group of esters takes place much less readily than among those of the acetic and malonic series; in consequence of this limitation, the yield of each product has been very far below that which might reasonably have been expected, especially in the case of α-triazoethylacetoacetic ester.

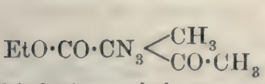
In reviewing the behaviour which characterises the azoimides of the acetoacetic series, it is convenient to recall their relationship with ethyl triazoacetate by means of the following formulæ:


$$EtO\cdot CO\cdot CN_3<\begin{matrix}H\\H\end{matrix}$$

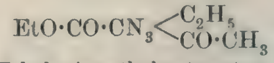
Ethyl triazoacetate.


$$EtO\cdot CO\cdot CN_3<\begin{matrix}H\\CO\cdot CH_3\end{matrix}$$

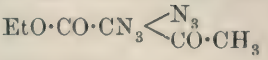
Ethyl triazoacetoacetate (not isolated).


$$EtO\cdot CO\cdot CN_3<\begin{matrix}CH_3\\CO\cdot CH_3\end{matrix}$$

Ethyl triazomethylacetoacetate.


$$EtO\cdot CO\cdot CN_3<\begin{matrix}C_2H_5\\CO\cdot CH_3\end{matrix}$$

Ethyl triazoethylacetoacetate.


$$EtO\cdot CO\cdot CN_3<\begin{matrix}N_3\\CO\cdot CH_3\end{matrix}$$

Ethyl bistriazoacetoacetate.

From this it appears that the effect of introducing an acetyl group into the triazoacetic ester molecule corresponds with that produced by the carboxyethyl radicle, the secondary character of triazotised carbon in both triazomalonic and triazoacetoacetic esters rendering these compounds too unstable for isolation. If, however, the remaining hydrogen in the latter substance is replaced by an alkyl group, stability is restored, but the resulting esters, unlike those of the triazomalonic series, cannot be made to yield the parent acids, owing to the readiness with which disruption of the chain takes place in the direction of either ketone or acid hydrolysis. Nevertheless, the study of these compounds has furnished an illustration of the stability which characterises even a triazo-ketone when the triazotised carbon atom is tertiary. The esters in question may be regarded as substitution products of triazoacetone in which the methylenic hydrogen has been completely replaced, and therefore represent a new type; when compared with triazoacetone, triazobutanones, phenacylazoimide, and α-triazocamphor, the dependence of such triazo-ketones upon hydrogen for the transformation which characterises their behaviour towards alkali hydroxide is clearly indicated. As noticed already in the substituted triazomalonic series, the liberation of nitrogen by the action of potassium hydroxide is only consequent on hydrolysis followed by loss of carbon dioxide,

$$\mathrm{CH_3\cdot CO\cdot CN_3(CH_3)\cdot CO_2\cdot C_2H_5} \longrightarrow \mathrm{CH_3\cdot CO\cdot CN_3(CH_3)\cdot CO_2K} \longrightarrow \mathrm{CHN_3(CH_3)\cdot CO_2K},$$

a substituted α-triazoacetic acid being formed. The action of ammonia on α-triazomethylacetoacetic ester establishes this point, as the product has been identified with α-triazopropionamide:

$$\mathrm{CH_3\cdot CO\cdot CN_3(CH_3)\cdot CO_2\cdot C_2H_5 + NH_4\cdot OH} = \mathrm{CH_3\cdot CO_2H + CH_3\cdot CHN_3\cdot CO\cdot NH_2 + C_2H_6O}.$$

Whilst this change illustrates the result of "acid hydrolysis," the alternative decomposition of acetoacetic derivatives, namely, "ketone hydrolysis," has been effected by means of hydrochloric acid, incidentally bringing to light a new reaction for triazo-ketones of the aliphatic series. On shaking α-triazomethylacetoacetic ester with hydrochloric acid (D 1·2), gas is slowly liberated, crystals of ammonium chloride separate, and a clear, bright yellow solution is produced. This must be ascribed to the following changes:

$$\mathrm{CH_3\cdot CO\cdot CN_3(CH_3)\cdot CO_2\cdot C_2H_5} \longrightarrow \mathrm{CH_3\cdot CO\cdot CN_3(CH_3)\cdot CO_2H} \longrightarrow \mathrm{CH_3\cdot CO\cdot CHN_3\cdot CH_3} \longrightarrow \mathrm{CH_3\cdot CO\cdot C(:NH)\cdot CH_3} \longrightarrow \mathrm{CH_3\cdot CO\cdot CO\cdot CH_3},$$

because diacetyl has been recognised as the final product. The alteration of a triazo-ketone indicated by this series of reactions has not been observed before, but there seems to be no doubt that it is the proper interpretation of the appearance of diacetyl, as we find that triazoacetone itself effervesces vigorously with concentrated hydrochloric acid, quickly yielding crystals of ammonium chloride; under the same treatment triazoacetic ester is merely hydrolysed, without giving nitrogen or ammonia.

A curious point of difference between the triazo-group and a similarly situated chlorine atom follows from the action of semicarbazide on ethyl α-triazomethylacetoacetate, which is converted into the semicarbazone, $CH_3\cdot C(:N\cdot NH\cdot CO\cdot NH_2)\cdot CN_3(CH_3)\cdot CO_2\cdot C_2H_5$; on exposing the parent chloro-derivative to the same agent, the product was found to have lost the halogen, and as we have not met with any description of the interaction between semicarbazide and the chloro-derivatives of substituted acetoacetic esters, the matter seems to deserve further study in connexion with the influence of negative groups on the formation of semicarbazones (Rupe and Kessler, *Ber.*, 1909, **42**, 4715).

A general comparison between the azoimides of the acetoacetic series and those of the malonic group shows the β-ketonic esters to be less easily obtainable, and less stable when produced, than the dicarboxylic esters. Particularly noticeable is this in the case of αα-bistriazoacetoacetic ester. Whilst the specimen of bistriazomalonic ester has remained clear and limpid during nine months in darkness, αα-bistriazoacetoacetic ester, within four days after distillation, deposited a mass of colourless crystals which have been identified with the substance spontaneously separating from bistriazoacetic ester (m. p. 91°). From this it is evident that the tendency to break up into acetic acid and disubstituted acetic ester,

$$CH_3CO\cdot C(N_3)_2\cdot CO_2\cdot C_2H_5 + H_2O = CH_3\cdot CO_2H + CH(N_3)_2\cdot CO_2\cdot C_2H_5,$$

is even more pronounced on the part of αα-bistriazoacetoacetic ester than in the case of αα-dichloroacetoacetic ester, which yields dichloroacetic ester with alkalis and ammonia, but is comparatively stable in absence of these agents. Furthermore, in preparing bistriazoacetoacetic ester, it was noticed that a considerable proportion of dichloroacetic ester accompanied the substance, and this circumstance, together with the rapid change undergone by the bistriazo-compound, would explain the very disappointing yield of the latter material. In view of the foregoing remarks it is not surprising to find that αα-bistriazoacetoacetic ester, when treated with alkali hydroxide, gives rise to potassium cyanide in association with the azide, as the formation of prussic acid has been connected hitherto with only those bistriazo-compounds in which both azidic groups are attached to the same carbon atom.

EXPERIMENTAL.

Attempts to Prepare Ethyl Triazoacetoacetate.

The interaction of α-chloroacetoacetic ester and sodium azide in aqueous alcohol recalled the experiences connected with attempts to prepare triazomalonic ester (this vol., p. 130); evidence of the production of a triazo-compound was given, but the material appeared to be very easily decomposed by water, and we therefore failed to separate it from its products of change and from the unaltered chloro-ester. There does not appear to be any action when dry sodium azide is shaken with an ethereal solution of ethyl chloroacetoacetate, and the change which takes place on removing the solvent is too profound, even at moderate temperatures, to encourage any hope that the α-triazoacetoacetic ester might be isolated.

Methyl α-Triazomethylacetoacetate, $CH_3 \cdot CO \cdot CN_3(CH_3) \cdot CO_2 \cdot CH_3$.

The chloro-ester required for the preparation of this material does not appear to have been described.

Methyl α-Chloromethylacetoacetate, $CH_3 \cdot CO \cdot CCl(CH_3) \cdot CO_2 \cdot CH_3$, was produced on adding sulphuryl chloride (34 grams) drop by drop to methyl methylacetoacetate (32 grams) at zero, the liquid being then allowed to take the temperature of the laboratory; after an interval of twelve hours it was heated one hour on the water-bath, poured into water, and extracted with ether, the solution being shaken with small quantities of water until no longer acid. The residue from the dried extract was distilled at 75—76°/13 mm., yielding 31 grams:

0·1253 gave 0·1100 AgCl. Cl = 21·86.

$C_6H_9O_3Cl$ requires Cl = 21·54 per cent.

The ester is a colourless liquid, having a faint odour of peppermint.

Preliminary experiments showed that replacement of chlorine by the triazo-group does not take place very readily in this series when the hydrogen of the methylene group is entirely substituted; merely shaking the chloro-ester with alcohol and aqueous sodium azide during twenty-four hours gave a product consisting mostly of unchanged material, although a certain proportion of the triazo-derivative was indicated by its behaviour towards potassium hydroxide, stannous chloride, and concentrated sulphuric acid; this was borne out by analysis, which showed that transformation to the extent of about 40 per cent. had taken place. The product from methyl α-chloromethylacetoacetate, which had been shaken during twenty hours with 25 grams of sodium azide and the necessary amount of water and alcohol to form a clear solution, was separated in the usual manner and shaken during a further period of twenty hours with 20 grams of sodium azide; as it still contained chlorine and an insufficient percentage of nitrogen, it was heated under reflux during five hours with the alcoholic liquid still containing sodium azide, and finally salted out with ammonium sulphate. Distillation of the dried liquid revealed a mixture, although there was no longer any chlorine present. A specimen of the pure triazo-ester was ultimately obtained by heating 34 grams of the chloro-ester in absolute alcohol with 20 grams of sodium azide in water during thirty hours under reflux. Here it was noticed that the proportion of first runnings was considerable, but 12 grams of a less volatile fraction distilled at 75—76°/0·66 mm.:

0·1208 gave 25·7 c.c. N_2 at 18° and 756 mm. N=24·44.
0·1625 „ 34·4 c.c. N_2 „ 17° „ 764 mm. N=24·69.
$C_6H_9O_3N_3$ requires N=24·56 per cent.

The ester is a colourless liquid without characteristic odour until warmed with water, when it develops a fragrant perfume, quite distinct from the peppermint suggested by the chloro-ester; it does not explode on a hot plate, and becomes only pale yellow during the lapse of several months if protected from light. Its sp. gr. is 1·1453 at 21°/21°. The effervescence with stannous chloride in hydrochloric acid is vigorous, and yields two-thirds the azidic nitrogen:

0·1738 gave 24·8 c.c. N_2 at 18° and 763 mm. N=16·29.
$C_6H_9O_3N_3$ requires $\frac{2}{3}$N=16·37 per cent.

Concentrated sulphuric acid also decomposes the substance, but not violently, whilst 30 per cent. aqueous potassium hydroxide effects hydrolysis at first without effervescence, although liberation of nitrogen occurs on heating the liquid, which is then found to contain only a trace of azide, without cyanide. Ferric chloride does not develop a coloration with the ester.

Ethyl α-Triazomethylacetoacetate, $CH_3{\cdot}CO{\cdot}CN_3(CH_3){\cdot}CO_2{\cdot}C_2H_5$.

The ethyl α-chloromethylacetoacetate required for the preparation of this material was obtained in the manner described by Roubleff (*Annalen*, 1890, **259**, 254); it was distilled at 82°/15 mm.

The chloro-ester (35 grams) in alcohol was heated with sodium azide (15 grams) in water during fifty to sixty hours under reflux, the product being precipitated with water and ammonium sulphate. As in the case of the methyl ester, there was a considerable proportion of first runnings following the complete removal of ether and alcohol, but the continued heating had displaced all chlorine; the purified ester boiled at 85°/1 mm.:

0·1987 gave 39·0 c.c. N_2 at 20° and 758 mm. N = 22·41.

$C_7H_{11}O_3N_3$ requires N = 22·70 per cent.

The substance resembles the methyl ester in all its properties, and has a sp. gr. of 1·1070 at 18°/18°; it does not explode on a hot plate, and the vapour in steam, when inhaled, does not produce the throbbing effect in the head which characterises that of triazoacetic ester. There is not any development of colour with ferric chloride.

The *semicarbazone*, $CH_3\cdot C(\vdots N\cdot NH\cdot CO\cdot NH_2)\cdot CN_3(CH_3)\cdot CO_2\cdot C_2H_5$.—After mixing 3 grams of the ester in a few c.c. of alcohol with an aqueous solution of semicarbazide acetate prepared from 3 grams of the hydrochloride, lustrous, transparent prisms separated in the course of a few hours; recrystallisation from benzene gave silky, snow-white needles, melting at 122° to a pale magenta liquid:

0·2334 gave 0·3390 CO_2 and 0·1226 H_2O. C = 39·62; H = 5·88.

0·1019 „ 31·6 c.c. N_2 at 25° and 760 mm. N = 34·60.

$C_8H_{14}O_3N_6$ requires C = 39·67; H = 5·78; N = 34·71 per cent.

The substance is freely soluble in acetone or chloroform, and dissolves readily in hot water, crystallising in long, lustrous needles on cooling; it is insoluble in boiling petroleum, and dissolves sparingly in cold benzene, but 1 gram requires only 3 c.c. of the hot solvent. Effervescence with concentrated sulphuric acid is very sluggish, but when stannous chloride is added to a suspension in dilute hydrochloric acid, nitrogen is liberated immediately, a clear solution being formed:

0·1208 gave 12·0 c.c. N_2 at 25° and 760 mm. N = 11·34.

$C_8H_{14}O_3N_6$ requires $\frac{1}{3}$N = 11·53 per cent.

Aqueous 30 per cent. potassium hydroxide forms a clear, yellow solution, which becomes colourless on boiling; ammonia is thereupon liberated, and potassium azide produced.

Ethyl α-Triazoethylacetoacetate, $CH_3\cdot CO\cdot CN_3(C_2H_5)\cdot CO_2\cdot C_2H_5$.

Ethyl α-chloroethylacetoacetate was first prepared by Conrad (*Annalen*, 1877, **186**, 241) from ethylacetoacetic ester and chlorine, whilst Isbert (*Annalen*, 1886, **234**, 187) employed phosphorus pentachloride; we used sulphuryl chloride, as recommended by Roubleff (*loc. cit.*) for the corresponding methyl derivative. From 50 grams of ethylacetoacetic ethyl ester and 44 grams of sulphuryl chloride, 45 grams of the chloro-ester, boiling at 90°/11 mm. and 64°/0·33 mm., were obtained.

The difficulty experienced in transforming the chloromethylacetoacetate was accentuated in the case of the ethyl derivative, and after several unsuccessful experiments it was found necessary to heat the ester in alcohol with aqueous sodium azide under reflux during upwards of one hundred hours before exchange of halogen for the triazo-group appeared to be complete. This protracted treatment naturally led to a considerable degree of subsidiary decomposition, which was indicated by the separation of a large earlier fraction when the product was distilled; from 40 grams of chloro-ester only 10 grams were collected at 84—85°/0·9 mm., although the same quantity of first runnings contained but a trace of chlorine:

0·1501 gave 28·2 c.c. N_2 at 21° and 764 mm. N = 21·49.

$C_8H_{13}O_3N_3$ requires N = 21·11 per cent.

The ester has a very faint odour, which becomes strong and fragrant in steam; it does not explode on a hot plate, and is quite stable when protected from light. It has a sp. gr. of 1·0536/19°. The action with concentrated sulphuric acid is very vigorous, whilst stannous chloride acts slowly; aqueous potassium hydroxide first hydrolyses the ester and liberates gas on heating, but does not produce either hydrazoic or prussic acid. Ferric chloride is without action on the ester.

The *semicarbazone*, $CH_3\cdot C(:N\cdot NH\cdot CO\cdot NH_2)\cdot CN_3(C_2H_5)\cdot CO_2\cdot C_2H_5$, separated more slowly than that of the methyl derivative, and was much more readily soluble in benzene, from which it crystallised in transparent plates, retaining the solvent, and melting indefinitely at about 130° (N = 30·52; $C_9H_{16}O_3N_6$ requires N = 32·81). On recrystallisation from boiling water, the hydrocarbon was liberated, and there separated long, lustrous needles, melting at 135°:

0·1361 gave 39·0 c.c. N_2 at 23° and 754 mm. N = 32·04.

$C_9H_{16}O_3N_6 + \frac{1}{2}H_2O$ requires N = 31·70 per cent.

The presence of the triazo-group was demonstrated by stannous chloride, concentrated sulphuric acid, and aqueous potassium hydroxide, the last-named decomposing the substance when heated, producing a transient yellow coloration, and liberating ammonia.

Acid and Ketone Hydrolysis of Ethyl α-Triazomethylacetoacetate.

The production of nitrogen when the alkylacetoacetic azoimides are heated with aqueous potassium hydroxide is doubtless due to "acid hydrolysis," which should give rise to the corresponding alkyltriazoacetic acid; when shaken with cold 30 per cent. aqueous potassium hydroxide, the ethyl ester of α-triazomethylacetoacetic acid quickly formed a clear solution, and, after acidification, the residue from the ethereal extract had the rancid odour of α-triazopropionic acid, and did not develop colour with ferric chloride. More definite evidence that the decomposition takes this direction is furnished by the action of ammonia. Two grams of ethyl α-triazomethylacetoacetate were shaken at zero with 10 c.c. of concentrated ammonia until a clear solution was formed, this being kept in a vacuum desiccator until crystals appeared; the product was recrystallised from benzene, and melted at 80° without depressing the melting point of triazopropionamide prepared from ethyl α-triazopropionate and ammonia (Trans., 1908, **93**, 673).

The course of the "ketone hydrolysis" is shown by the behaviour of α-triazomethylacetoacetic ester towards concentrated hydrochloric acid. One gram was shaken at intervals with 5 c.c. of this agent, when the liquid slowly became yellow and evolved gas; after many hours, crystals of ammonium chloride separated, and on diluting with water and extracting with ether, the residue from the latter was shown to contain diacetyl by means of the test described by Sachs and Rohmer (*Ber.*, 1902, **35**, 3311). The reaction in question does not appear to be well known, but it offers a very simple and striking method of recognising the diketone, which is mixed with common benzene containing thiophen, and treated with concentrated sulphuric acid; a very intense dark green coloration is developed when diacetyl is present.

Ethyl αα-Bistriazoacetoacetate, $CH_3\cdot CO\cdot C(N_3)_2\cdot CO_2\cdot C_2H_5$.

Much time and material has been spent in attempting to isolate the bistriazo-ester, and although a small quantity of the substance has been obtained on two occasions, it is accompanied by a mixture of more volatile compounds, of which the principal constituent is ethyl dichloroacetate, due to disruption of the dichloroacetoacetic molecule prior to double decomposition with sodium azide.

αα-Dichloroacetoacetic ester (25 grams) in alcohol (40 c.c.) was shaken at frequent intervals during six days with 25 per cent. aqueous sodium azide (100 grams); hydrazoic acid was liberated freely, and when the residue from ether extraction was distilled under reduced pressure, a considerable proportion of a colourless, pungent liquid passed over, 5 grams boiling steadily at 61—64°/25 mm. This did not effervesce with concentrated sulphuric acid, and was identified with ethyl dichloroacetate by conversion into the amide, which did not depress the melting point of dichloroacetamide when mixed with that substance. The residue from the initial distillation was then heated under 0·9 mm. pressure, yielding 1·2 grams at 81—82°, and leaving a few drops of pale brown material which became crystalline on cooling. The distillate had a more pungent and distinctive odour than that of the triazoacetoacetic esters described above; on one occasion the attempt to estimate nitrogen led to an explosion:

0·0659 gave 23·0 c.c. N_2 at 25° and 766 mm. N = 39·25.
$C_6H_8O_3N_6$ requires N = 39·62 per cent.

The ester does not develop colour with ferric chloride, even when heated, indicating that it is fairly stable. The decomposition with concentrated sulphuric acid is very violent, and brisk effervescence takes place with stannous chloride in hydrochloric acid. When shaken with 30 per cent. potassium hydroxide, the mixture becomes warm and liberates nitrogen steadily, but not in large quantity, and probably therefore the decomposition is due to preliminary "acid hydrolysis" leading to bistriazoacetic acid, in which the triazotised carbon, being secondary, loses the azoimide complex very readily; the clear alkaline liquid yields a further quantity of nitrogen when heated, and contains potassium azide and cyanide.

A more definite proof of transformation into bistriazoacetic ester is given by the alteration which αα-bistriazoacetoacetic ester undergoes with lapse of time. One c.c., preserved in darkness during six months, deposited a glassy crystal weighing 1 decigram; this melted at 91°, and when mixed with the similar substance deposited by bistriazoacetic ester (this vol., p. 130) melted still at that temperature. A second specimen of bistriazoacetoacetic ester changed into this crystalline compound within four days of being distilled, and it is no doubt in part due to this complete and rapid decomposition that the yield of the bistriazo-derivative is so small.

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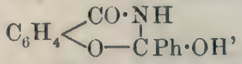
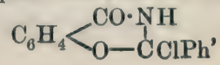
CXXVI.—6-*Chloro-2-phenyl-*1 : 3-*benzoxazine-*4-*one and Related Derivatives.*

By Arthur Walsh Titherley and Ernest Chislett Hughes.

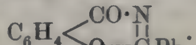
The cyclic hydroxyoxazone derivative,  $C_6H_4\Big<\begin{array}{l}CO\cdot NH\\ O-\overset{|}{C}Ph\cdot OH\end{array}$, intermediate in the reversible rearrangement of the two benzoylsalicylamides appears to be quite incapable of separate existence, and when produced by oxidation of 2-phenyldihydro-1:3-benzoxazine-4-one ("phenylbenzometoxazone") yields *N*-benzoylsalicylamide (Titherley, Trans., 1907, **91**, 1420). The object of the present investigation was to prepare the related 2-chloro-derivative,



$$C_6H_4\Big<\begin{array}{l}CO\cdot NH\\ O-\overset{|}{C}ClPh\end{array},$$

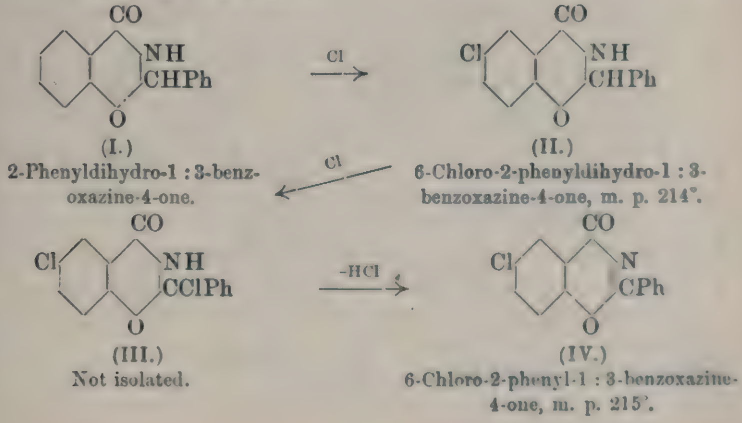
with a view to studying its behaviour when the chlorine atom was replaced by hydroxyl, and the mode of preparation attempted was the chlorination of 2-phenyldihydro-1 : 3-benzoxazine-4-one (I) in the expectation that the hydrogen atom in position 2 might be replaced by chlorine. A possible alternative reaction is that of substitution in the benzene nucleus.

The chlorination was carried out under a variety of conditions, but in no circumstances could the desired 2-chloro-derivative be obtained. While the work was in progress it became evident that this derivative, if formed, would be unstable, and immediately lose hydrogen chloride. One of the authors (Titherley, this vol., p. 200) has now shown that this 2-chloro-compound is probably produced as an intermediate product in the action of hydrogen chloride on either *O*- or *N*-benzoylsalicylamide, but that it at once loses hydrogen chloride, yielding the unsaturated compound, 2-phenyl-1 : 3-benzoxazine-4-one,



$C_6H_4<\substack{CO\cdot N \\ O-\overset{\|}{C}Ph}$.

An examination of the products of chlorination of the oxazone (I) under all conditions made it clear that the chlorine had substituted hydrogen in the benzene nucleus, and by working carefully it was possible to isolate two monochloro-derivatives of almost identical melting point (214—215°), the proportions of which varied with the time of chlorination. One of these, formed first, was shown to be a simple chloro-substitution derivative (II), and the other, the amount of which increased with time, was proved to be the chloro-derivative (IV) of the unsaturated cyclic compound recently described by Titherley (*loc. cit.*). It is evident that, although substitution first takes place in the benzene ring, the hydrogen atom at position 2 in the oxazone nucleus is subsequently replaced, giving the 2-chloro-derivative (III), which loses hydrogen chloride as fast as it is formed:



(I.) 2-Phenyldihydro-1 : 3-benzoxazine-4-one.

(II.) 6-Chloro-2-phenyldihydro-1 : 3-benzoxazine-4-one, m. p. 214°.

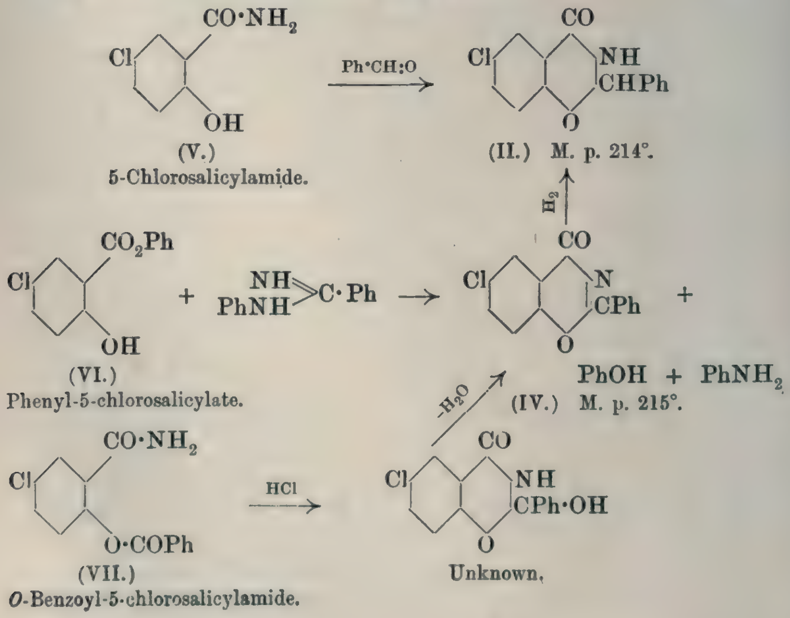
(III.) Not isolated.

(IV.) 6-Chloro-2-phenyl-1 : 3-benzoxazine-4-one, m. p. 215°.

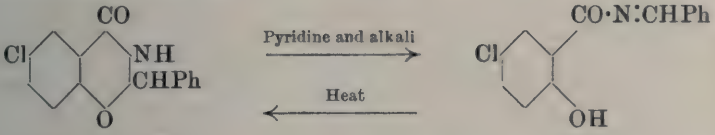
Owing to the great similarity in the physical properties of these two chloro-derivatives (II and IV), and the fact that they give practically the same figures for chlorine and nitrogen on analysis, considerable difficulty was encountered in isolating them and establishing their separate identity. Advantage was eventually taken of a marked difference in their velocities of formation in fixing the optimum conditions for the preparation of the two substances.

The position of the chlorine atom (6) in the two compounds was proved by the fact that, on alkali hydrolysis, 5-chlorosalicylamide (V) was produced; and the constitution of the compound (II) was confirmed by its independent synthesis by the condensation of 5-chlorosalicylamide and benzaldehyde (compare Titherley and Hicks, Trans., 1909, **95**, 915). Similarly, the constitution of the unsaturated cyclic compound (IV) was confirmed by its independent synthesis from phenyl-5-chlorosalicylate (VI) and phenylbenzamidine by a method similar to that by which 2-phenyl-1: 3-benzoxazine-4-one has been recently obtained from phenyl salicylate, as well as by the internal condensation of *O*-benzoyl-5-chlorosalicylamide (VII) under the catalytic influence of hydrogen chloride, similar to that of *O*-benzoylsalicylamide (compare Titherley, this vol., p. 200). Further, the relation between the two chloro-compounds has been confirmed by the fact that the unsaturated compound (IV), on reduction, is transformed into the dihydro-derivative (II).

These relations are indicated in the scheme:

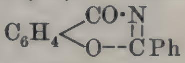


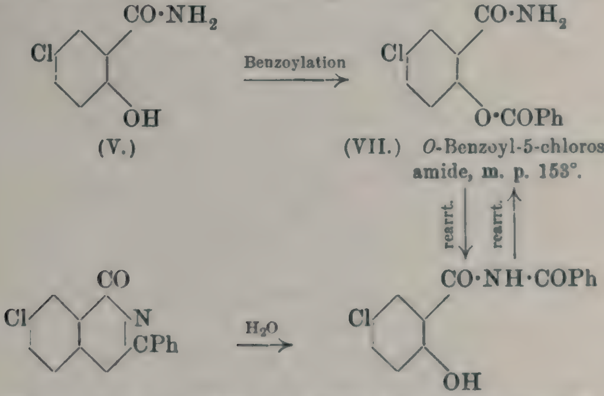
The two chloro-compounds (II and IV) differ strongly in their chemical properties, and whilst the dihydro-compound (II) on alkali hydrolysis at 100° yields benzaldehyde, the unsaturated ring compound (IV) yields benzoic acid. The dihydro-compound is similar throughout in its properties to its parent substance, "phenylbenzometoxazone," and on treatment with pyridine and alkali suffers a similar ring rupture (compare Titherley, Trans., 1907, **91**, 1420), yielding the isomeric *syn*-benzylidene-5-chlorosalicylamide (VIII), which is even more labile than the corresponding simple *syn*-benzylidenesalicylamide (*loc. cit.*), and rearranges readily into the cyclic compound (II):



(II.) M. p. 214°.

(VIII.) *syn*-Benzylidene-5-chlorosalicylamide.

The unsaturated chloro-derivative (IV) is similar in its chemical properties to the parent substance,  $C_6H_4<\begin{matrix}CO\cdot N\\ O{-}{-}CPh\end{matrix}$, but melts more than 100° higher, and is much less soluble in solvents. Moreover, it is much more stable in respect of the 1:3-oxazone ring, and whereas the parent compound is extremely sensitive to aqueous acids in the cold, the chloro-derivative (IV) is only slowly affected. On heating, however, it is easily ruptured with addition of water, giving *N*-benzoyl-5-chlorosalicylamide (IX), which has been shown to be identical with the rearrangement product (on melting) of *O*-benzoyl-5-chlorosalicylamide (VII). Conversely, the *N*-benzoyl derivative (IX) is rearranged to the *O*-benzoyl isomeride (VII) by



(V.)

(VII.) *O*-Benzoyl-5-chlorosalicylamide, m. p. 153°.

(IV.) M. p. 215°.

(IX.) *N*-Benzoyl-5-chlorosalicylamide, m. p. 238°.

boiling with acetic acid, and complete identity has been established between this *O*-benzoyl derivative and the product of pyridine-benzoylation of 5-chlorosalicylamide (V) at −15°.

The rearrangement phenomena are analogous in every particular to those observed between *O*- and *N*-benzoylsalicylamides by McConnan and Titherley (Trans., 1906, **89**, 1318), and the above relations are expressed in the scheme on p. 1371.

EXPERIMENTAL.

The Action of Chlorine on 2-Phenyldihydro-1 : 3-benzoxazine-4-one.

(*a*) *Without Solvent.*—A number of experiments were carried out without solvent at 110° and higher temperatures, both in bright daylight and in the dark. Illumination did not sensibly affect the course of the reaction. During the passage of the chlorine, the solid in the flask slowly melted, and after about an hour a yellow semi-solid mass resulted, which, after cooling, on treatment with cold benzene left a white, crystalline solid. The latter consisted of a mixture in varying proportions of 6-chloro-2-phenyldihydro-1 : 3-benzoxazine-4-one and 6-chloro-2-phenyl-1 : 3-benzoxazine-4-one, which were never completely separated by recrystallisation. The benzene filtrate, on keeping, deposited a solid, which gave a yellow ammonium and sodium salt. This solid, on investigation and analysis, was found to consist of *N*-benzoylsalicylamide and *N*-benzoyl-5-chlorosalicylamide (chiefly the latter) in proportions which varied with different experiments. These two compounds are evidently derived by the action of atmospheric moisture, under the catalytic influence of hydrogen chloride present in small quantity, on 2-phenyl-1 : 3-benzoxazine-4-one and its chloro-derivative formed as by-products in the chlorination.

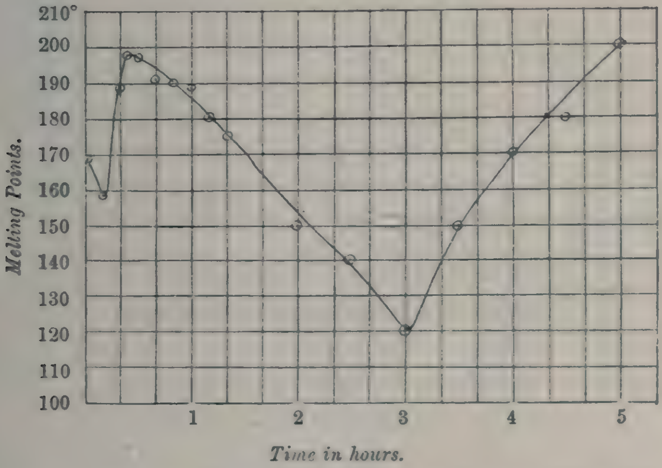
(*b*) *In Presence of Solvents.*—Chloroform and benzotrichloride were found to be the most suitable solvents for studying the chlorination at different temperatures (61° and 110°).

(1) *Using Chloroform.*—Dry chlorine was passed through a boiling solution of 5 grams of 2-phenyldihydro-1 : 3-benzoxazine-4-one in 50 grams of chloroform in the dark at a uniform rate of about 4 c.c. per second. At regular intervals a small quantity of the solution was withdrawn, allowed to evaporate on a watch-glass, and the melting point of the resulting solid after washing with cold benzene determined. By plotting the melting points against time, a curve (Fig. 1) was obtained.

The first rise corresponds to the production, with a high velocity, of 6-chloro-2-phenyldihydro-1 : 3-benzoxazine-4-one (m. p. 214°), which reached a maximum in twenty-two minutes. The subsequent depression, following its conversion with a low velocity into 6-chloro-2-phenyl-1 : 3-benzoxazine-4-one (m. p. 215°), corresponds with mixtures of the two substances, and the second maximum with the maximum production of the latter compound, melting at 215°. Both reactions take place side by side, and in any case are accompanied by secondary changes which have not been studied, but appear to lead to breaking up of the 1 : 3-oxazone ring. Hence the two products obtained at the respective melting-point maxima are not quite pure, although they are sufficiently so to be purified by recrystallisation. On the other hand, it was found to be almost impossible to separate them when mixed in proportions corresponding with points on the curve other than the maxima, and the conditions of preparation described on p. 1374 were based on the curve.

FIG. 1.

Chlorination in chloroform solution at 61°.

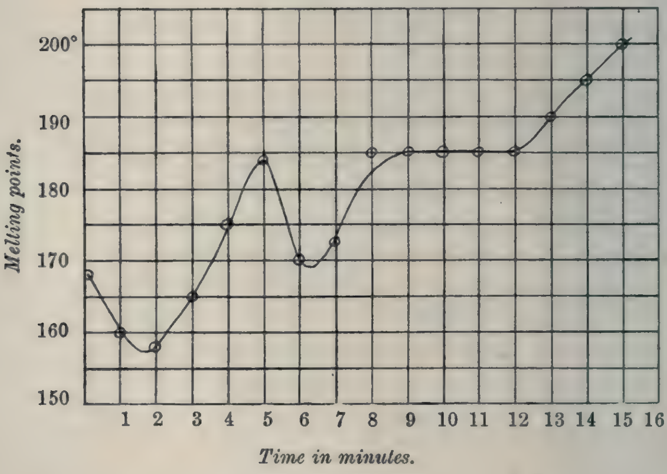


(2) *Using Benzotrichloride.*—Dry chlorine was passed into a solution of 5 grams of 2-phenyldihydro-1 : 3-benzoxazine-4-one in 7·5 grams of benzotrichloride at 110° in the dark at a uniform rate of 8 to 9 c.c. per second. The melting points of the solid, obtained from samples withdrawn at one minute intervals, are shown on the curve (Fig. 2), the mean temperature being given in the intervening readings between eight and twelve minutes, where the product melted over a range about 10°. As in the chloroform experiments, the curve shows two maxima, but the velocities of the two reactions are, of course, much higher.

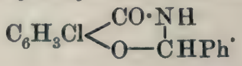
An examination of the product obtained at the first maximum showed that it consisted essentially of the chloro-derivative melting at 214°, whilst that obtained at the second maximum consisted essentially of the derivative melting at 215°, as in the case of the chloroform experiments, but owing to the increased velocity of the reactions at 110° it was found inconvenient to adopt the benzochloride process in the preparation of 6-chloro-2-phenyldihydro-1 : 3-benzoxazine-4-one (m. p. 214°), since it is difficult to stop the chlorination at exactly the right point. Chloroform was accordingly used in the preparation of this compound, and benzotrichloride was more conveniently used in the preparation of 6-chloro-2-phenyl-1 : 3-benzoxazine-4-one.

FIG. 2.

Chlorination in benzotrichloride solution at 110°.



6-*Chloro*-2-*phenyldihydro*-1 : 3-*benzoxazine*-4-*one*,


$$C_6H_3Cl<\begin{matrix}CO\cdot NH \\ \quad\;\; | \\ O—CHPh\end{matrix}.$$

(1) *Preparation by Chlorination Method.*—Dry chlorine was passed into a boiling solution of 20 grams of 2-phenyldihydro-1 : 3-benzoxazine-4-one in 200 c.c. of chloroform in a reflux apparatus. The action was conducted in a dark chamber, and the gas passed in for twenty minutes at the rate of about 6 c.c. per second, during which hydrogen chloride was liberated in large quantity. The impure chloro-derivative, which crystallised out as a white mass after cooling, weighed 12·5 grams, and melted between 195° and

200°. After recrystallisation four times from alcohol, it was obtained pure, the melting point remaining constant at 214°:

0·3816, by Kjeldahl's method, required 14·4 c.c. *N*/10-HCl. N = 5·28.

0·3048 gave 0·1700 AgCl. Cl = 13·77.

$C_{14}H_{10}O_2NCl$ requires N = 5·39; Cl = 13·69 per cent.

The compound is sparingly soluble in cold alcohol, benzene, or acetone. but readily so in hot alcohol, from which it crystallises in bundles of fine needles.

Hydrolysis. — 6-Chloro-2-phenyldihydro-1 : 3-benzoxazine-4-one is insoluble in cold dilute alkali, but is readily hydrolysed by the hot reagent, benzaldehyde being produced. One gram was boiled with 10 c.c. of 10 per cent. sodium hydroxide for five minutes, when the solid had completely disappeared. After cooling, alcohol was added, and then excess of dilute hydrochloric acid. After some time, a mass of fine needles separated, melting at 223—224°, which were shown to consist of 5-chlorosalicylamide, the substance being identical in all respects with that obtained (1) by the chlorination of salicylamide (see below), and (2) by pyridine-alkali hydrolysis of 6-chloro-2-phenyl-1 : 3-benzoxazine-4-one (p. 1377).

(2) *Synthetic Preparation of* 6-*Chloro-2-phenyldihydro*-1 : 3-*benzoxazine*-4-*one*.—The 5-chlorosalicylamide required for the synthesis has been described by Smith (*Ber.*, 1878, **11**, 1227), who obtained it from methyl 5-chlorosalicylate. It was prepared by the authors from salicylamide (50 grams in 1500 c.c. of boiling chloroform) by treating it with a rapid stream of dry chlorine in the dark for nearly an hour.

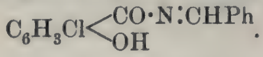
Twenty grams of 5-chlorosalicylamide were mixed with 50 grams of benzaldehyde, and the mixture, after addition of about 1 c.c. of alcoholic hydrogen chloride, was heated to 60—70° for thirty minutes. A clear solution resulted at first, which gradually deposited long, silky needles. On cooling, a mass of crystals was obtained, which were washed carefully with cold alcohol in order to remove the excess of benzaldehyde. The crystals consisted of pure 6-chloro-2-phenyldihydro-1 : 3-benzoxazine-4-one, and melted at 214°, the yield being 22 grams. After recrystallisation from alcohol, the melting point was raised to 215°, and the identity of the compound with that obtained by chlorination (m. p. 214°) was shown by careful comparison, and by the fact that a mixture of the two products melted sharply at 214°:

0·3854, by Kjeldahl's method, required 14·2 c.c. *N*/10-HCl. N = 5·21.

0·2084 gave 0·1152 AgCl. Cl = 13·67.

$C_{14}H_{10}O_2NCl$ requires N = 5·39; Cl = 13·69 per cent.

syn-*Benzylidene-5-chlorosalicylamide,*



$$C_6H_3Cl<\begin{matrix}CO\cdot N:CHPh\\OH\end{matrix}.$$

Five grams of 6-chloro-2-phenyldihydro-1 : 3-benzoxazine-4-one in 35 grams of pyridine were shaken with 40 c.c. of 10 per cent. sodium hydroxide for half an hour, by which time the bright yellow colour which at first developed had disappeared. The solution was diluted with water to 2 litres, and treated at 0° with excess of dilute hydrochloric acid. The resulting thick white precipitate, consisting of the *syn*-chloro-derivative, together with a little unchanged compound, was collected, dried in a vacuum and digested with 10 per cent. sodium hydroxide. In this way the very sparingly soluble sodium salt of the *syn*-chloro-derivative was produced, and the white solid, after washing with water to remove traces of 5-chlorosalicylamide (due to slight hydrolysis), was digested with a mixture of equal parts of alcohol and water, in which the sodium salt is readily soluble. The filtrate from the insoluble unchanged cyclic compound, on acidification, gave a white amorphous precipitate of the *syn*-chloro-derivative, which was dried on porous porcelain in a vacuum. It could not be crystallised from solvents without rearrangement to the cyclic isomeride, but analysis showed that it was practically pure:

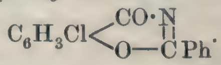
0·4284, by Kjeldahl's method, required 16·5 c.c. $N/10$-HCl. N = 5·40.

0·1766 gave 0·0948 AgCl. Cl = 13·30.

$C_{14}H_{10}O_2NCl$ requires N = 5·39; Cl = 13·69 per cent.

The compound is very sparingly soluble in all solvents except hot alcohol (with rearrangement). It melts at about 150°, also with rapid and complete rearrangement, to 6-chloro-2-phenyldihydro-1 : 3-benzoxazine-4-one, which solidifies in the tube and then melts at 213°. The compound gives a purple coloration in acetone solution with alcoholic ferric chloride.

6-*Chloro-2-phenyl*-1 : 3-*benzoxazine*-4-*one,*



$$C_6H_3Cl<\begin{matrix}CO\cdot N\\ \quad\ \ \|\\O-CPh\end{matrix}.$$

(1) *Preparation by Chlorination Method.*—A rapid stream of dry chlorine (8 to 9 c.c. per second) was passed into a solution of 10 grams of 2-phenyldihydro-1 : 3-benzoxazine-4-one in 15 grams of benzotrichloride at 110° in the dark for thirty minutes. On cooling, a mass of fine white needles separated after some time, which were collected and washed with small quantities of cold benzene. After recrystallisation, first from benzene and finally from acetone, the

pure compound was obtained in long silky needles, melting at 215°. (When not quite pure, the compound crystallises in much shorter needles.) The yield was 7 grams:

0·4327, by Kjeldahl's method, required 16·5 c.c. *N*/10-HCl. N = 5·24.

0·2266 gave 0·1288 AgCl. Cl = 14·06.

$C_{14}H_8O_2NCl$ requires N = 5·43; Cl = 13·78 per cent.

The compound is somewhat sparingly soluble in hot alcohol, readily so in hot benzene or acetone, but sparingly so in the usual organic solvents in the cold. It is not affected by cold dilute sodium hydroxide, but in contact with strong aqueous ammonia it yields fine orange-yellow needles, which are under investigation. The compound is not sensibly affected by cold dilute acids, but in hot alcoholic solution with a little hydrochloric acid, it rapidly undergoes disruption with absorption of water, yielding *N*-benzoyl-5-chlorosalicylamide (m. p. 235°), which separates from the hot liquid as a voluminous microcrystalline mass if the solution is not too dilute. The yield was practically quantitative:

0·2994, by Kjeldahl's method, required 11·8 c.c. *N*/10-HCl. N = 5·26.

0·2468 gave 0·1234 AgCl. Cl = 12·37.

$C_{14}H_{10}O_3NCl$ requires N = 5·08; Cl = 12·88 per cent.

The substance was identical with the synthetically prepared *N*-benzoyl-5-chlorosalicylamide (p. 1380).

Hydrolysis of 6-*Chloro*-2-*phenyl*-1 : 3-*benzoxazine*-4-*one.*

One gram was dissolved in 3 grams of pyridine by warming, and the solution cooled quickly in order to obtain the compound in a fine state of division. The mixture was then treated with 0·5 gram of sodium hydroxide in 100 c.c. of water, and the temperature was raised to 100°. An intense yellow colour developed (due to the sodium salt of *N*-benzoyl-5-chlorosalicylamide), which after a few minutes disappeared. The colourless solution was then rapidly cooled, diluted to 300 c.c., and acidified. The precipitated 5-chlorosalicylamide weighed 0·64 gram (theory requires 0·665), and the filtrate, after adding salt and extracting with ether, gave 0·45 gram of benzoic acid melting, after recrystallisation, at 119° (theory requires 0·47). The 5-chlorosalicylamide, after recrystallisation from alcohol, was obtained in fine needles, melting at 224—225°:

0·4414, by Kjeldahl's method, required 25·4 c.c. *N*/10-HCl. N = 8·05.

0·2800 gave 0·2374 AgCl. Cl = 20·94.

$C_7H_6O_2NCl$ requires N = 8·16; Cl = 20·70 per cent.

The melting point was not depressed when mixed with the product obtained by chlorinating salicylamide (p. 1375). Further, the position (5) of the chlorine atom was confirmed by prolonged hydrolysis at 100° with sodium hydroxide, the 5-chlorosalicylic acid described by Hübner and Brenken (*Ber.*, 1873, **6**, 1227) being obtained.

Reduction of 6-*Chloro*-2-*phenyl*-1 : 3-*benzoxazine*-4-*one.*

Owing to the sparing solubility of the substance in alcohol or ether, the method of reduction, using aluminium amalgam employed by Titherley (*loc. cit.*) for the parent compound, failed in spite of numerous trials. The following method gave excellent results. One gram of the substance, dissolved in 100 c.c. of pure acetic acid, was treated in the cold with 1·5 grams of zinc dust, and shaken for an hour. After filtering, the clear solution was diluted to 500 c.c. with water, when 6-chloro-2-phenyldihydro-1 : 3-benzoxazine-4-one separated as a white microcrystalline precipitate. It was quite pure, and melted at 213—214°, and a mixture with the synthetic substance (p. 1375) melted at 213—214°. It gave benzaldehyde on hydrolysis, and the yield was 0·7 gram:

0·1176, by Kjeldahl's method, required 4·6 c.c. *N*/10-HCl. N = 5·47.

0·1382 gave 0·0806 AgCl. Cl = 14·4.

$C_{14}H_{10}O_2NCl$ requires N = 5·39; Cl = 13·69 per cent.

(2) *Synthetic Preparation of* 6-*Chloro*-2-*phenyl*-1 : 3-*benzoxazine*-4-*one.*—The synthesis was effected from phenylbenzamidine and phenyl 5-chlorosalicylate; the latter compound described by Curatolo (*Gazzetta*, 1898, **28**, i, 154) being prepared by a modified method, using chloroform instead of alcohol as a solvent.

Seven grams of phenyl 5-chlorosalicylate and 5 grams of phenylbenzamidine were heated together at 110° for four hours. A clear, yellow oil resulted, which eventually solidified to a large extent, phenol and aniline being liberated as the reaction proceeded. After cooling, the product was extracted with small quantities of benzene to remove phenol and aniline, together with a bright yellow substance, which appeared to be 5-chlorosalicylphenylbenzamidine, $OH\cdot C_6H_3Cl\cdot CO\cdot NH\cdot CPh\dot{:}NPh$, but was not isolated. This substance is evidently the first condensation product in the reaction between phenyl 5-chlorosalicylate and phenylbenzamidine (compare Titherley, this vol., p. 204), and by reversible decomposition with loss of aniline yields 6-chloro-2-phenyl-1 : 3-benzoxazine-4-one, which, on account of its high melting point, separates out as the solid above mentioned. The solid, after washing with benzene, became white, and on recrystallising, first from hot benzene and finally from acetone, the compound was obtained quite pure in colourless silky needles, melting at 215°. It was identical in properties with the compound prepared by chlorination (p. 1376):

0·3841, by Kjeldahl's method, required 15·0 c.c. *N*/10-HCl. N = 5·46.

0·1688 gave 0·0946 AgCl. Cl = 13·86.

$C_{14}H_8O_2NCl$ requires N = 5·43; Cl = 13·78 per cent.

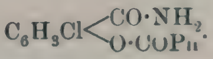
(3) *Preparation of* 6-*Chloro*-2-*phenyl*-1 : 3-*benzoxazine*-4-*one from* O-*Benzoyl*-5-*chlorosalicylamide*.—The method employed was similar to that adopted by Titherley (this vol., p. 208), anisole instead of xylene being used as a solvent. One gram of *O*-benzoyl-5-chlorosalicylamide (see below) in 10 c.c. of anisole was treated at 150° in a small distilling flask with a slow stream of dry hydrogen chloride for three minutes, and the anisole carrying the chemically-formed water slowly distilled off. A yellow syrup remained, which solidified on cooling. By extracting with boiling benzene from a small quantity (0·09 gram) of insoluble *N*-benzoyl-5-chlorosalicylamide, a filtrate was obtained which, on cooling, deposited 6-chloro-2-phenyl-1 : 3-benzoxazine-4-one in a nearly pure condition, melting at 214°, and weighing 0·8 gram. It was obtained quite pure (m. p. 215°) by a single recrystallisation from acetone, and was found to be identical in all respects with the product obtained by the previous methods:

0·3660, by Kjeldahl's method, required 14·3 c.c. *N*/10-HCl. N = 5·45.

0·3148 gave 0·1752 AgCl. Cl = 13·76.

$C_{14}H_8O_2NCl$ requires N = 5·43; Cl = 13·78 per cent.

O-*Benzoyl*-5-*chlorosalicylamide*,



$C_6H_3Cl<\begin{matrix}CO\cdot NH_2\\ O\cdot COPh\end{matrix}$.

A solution of 20 grams of 5-chlorosalicylamide in 40 grams of pyridine (dried by barium oxide) was treated with 20 grams of benzoyl chloride with continual shaking. The temperature was kept at −15° during the addition, which occupied three hours, and the resulting bright red mixture was kept at −15° for a further hour. It was then shaken with 100 c.c. of dry ether, the ethereal pyridine solution decanted off, and the remaining yellow solid mass treated with dilute sulphuric acid at 0°. The insoluble biscuit-coloured powder which remained, consisting of the crude *O*-benzoyl derivative, after washing with water and ether, weighed 22 grams, and melted at 150°. On recrystallisation from toluene, it separated in fine colourless needles, melting at 153°:

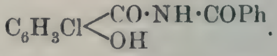
0·5902, by Kjeldahl's method, required 21·8 c.c. *N*/10-HCl. N = 5·16.

0·3092 gave 0·1636 AgCl. Cl = 13·08.

$C_{14}H_{10}O_3NCl$ requires N = 5·08; Cl = 12·88 per cent.

O-*Benzoyl*-5-*chlorosalicylamide* is sparingly soluble in the common organic solvents in the cold. In boiling alcohol it dissolves, but is rapidly rearranged to *N*-benzoyl-5-chlorosalicylamide, which separates from the hot liquid. The same rearrangement occurs on boiling with water, or on melting, and the clear liquid obtained by fusion at 153° sets in about thirty seconds to the solid *N*-benzoyl derivative, which then melts at about 235°.

N-*Benzoyl*-5-*chlorosalicylamide*,



$C_6H_3Cl{<}\substack{CO\cdot NH\cdot COPh\\ OH}$.

Two grams (accurately weighed) of *O*-benzoyl-5-chlorosalicylamide were dissolved in the minimum quantity of boiling alcohol, the solution was diluted with 200 c.c. of water at 80°, and the temperature kept at the boiling point for a few minutes. A white, voluminous, microcrystalline precipitate of the pure *N*-benzoyl derivative was obtained, melting sharply at 238°, and weighing 1·967 gram (theory requires 2 grams). The melting point was not changed by recrystallisation from boiling anisole:

0·3720, by Kjeldahl's method, required 13·9 c.c. *N*/10-HCl. N = 5·23.

0·2054 gave 0·1094 AgCl. Cl = 13·1.

$C_{14}H_{10}O_3NCl$ requires N = 5·08; Cl = 12·88 per cent.

The identity of the compound with the product of hydrolytic rupture of the unsaturated cyclic derivative (p. 1377) was shown by a comparison of the physical and chemical properties, and a mixture of the two specimens melted at 237°.

N-*Benzoyl*-5-*chlorosalicylamide* is very sparingly soluble in all solvents, cold or hot. It may be recrystallised from boiling acetic acid if the operation is rapidly carried out to avoid rearrangement (see below). In all its properties it is very similar to *N*-benzoylsalicylamide, and like it, forms intense yellow sparingly soluble sodium and ammonium salts, from which in aqueous solution acids precipitate the substance in colourless gelatinous form.

With alkali at 100° it is readily hydrolysed, yielding benzoic acid and 5-chlorosalicylamide (m. p. 224°).

Rearrangement. — Like *N*-benzoylsalicylamide, the 5-chloro-derivative, on boiling with acetic acid, suffers a reversible rearrangement to the *O*-benzoyl isomeride. One gram was boiled with 25 grams of pure acetic acid for four hours; on cooling, 0·2 gram of unchanged *N*-benzoyl derivative separated out, and on diluting the filtrate with water 0·7 gram of *O*-benzoyl-5-chlorosalicylamide was obtained (m. p. 148°), which, after recrystallisation from toluene, melted at 151°. Its properties were identical with those of the synthetic product (p. 1379).

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CXXVII.—*The Alkaloids of the Pukatea.*

By BERNARD CRACROFT ASTON.

THE Pukatea (*Laurelia Novae Zealandiae*), one of the most characteristic trees of the northern part of New Zealand, belongs to the *Monimiaceae*—a small family, most largely represented in the tropics. The genus is confined to South America and New Zealand.

The aromatic nature of the pukatea, and the fact that decoctions of the bark are used by the Maoris for alleviating various disorders, have suggested that the tree contains compounds possibly of medicinal value (see Colenso, *Trans. N.Z. Inst.*, 1868, **1**, 51; and Goldie, *ibid.*, 1904, **38**, 118).

Attention was first drawn by the author (*N. Z. Dept. of Agriculture, Annual Report*, 1901, p. 284) to the occurrence of alkaloids in the tree, and the peculiar property possessed by the bark of causing, when chewed, a tingling sensation on the tongue was traced to a crystalline alkaloid of definite melting point. More recently the investigation of the bark has been continued. The alkaloid, for which the name *pukateine* is proposed, melts at 200°, and has the composition and molecular weight corresponding with the formula $C_{17}H_{17}O_3N$. In the mother liquors obtained in the extraction of pukateine, two other alkaloids are present. Neither of these bases has been obtained in the crystalline state, but the salts of one, for which the name *laureline* ($C_{19}H_{21}O_3N$) is proposed, crystallise well. The third alkaloid, for which the name *laurepukine* is suggested, has been obtained only as an amorphous powder.

EXPERIMENTAL.

Isolation of the Alkaloids.

Seventy-five kilos of bark, freshly collected in the month of July from trees in the Marlborough Sounds, were finely divided and steeped for seven days in alcohol containing 0·5 per cent. of acetic acid. The alcohol was then pressed off, and this treatment of the bark was repeated three times. From the 98 litres of extract thus obtained, the alcohol was distilled, and the remaining acid aqueous liquors were diluted with boiling water and filtered. The acid filtrate was thoroughly shaken with chloroform, which removed two feebly-basic alkaloids. One of these, pukateine, is sparingly soluble in cold alcohol, and was obtained in an almost pure state when the residue from the distillation of the chloroform was stirred with alcohol and kept for some hours.

The second alkaloid, laureline, remained in solution as acetate in the alcohol from which the pukateine had crystallised. The amorphous residue left on evaporating the still acid alcohol was boiled with dilute sulphuric acid, and the hot solution filtered. The sparingly soluble sulphate of laureline crystallised in the filtrate on cooling (pukateine sulphate is easily soluble in dilute sulphuric acid).

A third alkaloid (laurepukine) remained in the acid aqueous liquor from which the acetates of pukateine and laureline had been extracted by chloroform. Sodium hydroxide precipitated the crude alkaloid in the amorphous condition.

A sample of the crushed bark was found to contain 0·7 per cent. of approximately pure pukateine—a yield not realised on a large scale, as only 64 grams of the alkaloid were obtained from the 75 kilos. of bark. The content of pukateine appeared to vary at different times of the year. If the bark was allowed to remain in a dry room some months before extraction, the yield was very small.

Pukateine.

Pure pukateine, $C_{17}H_{17}O_3N$, is a white, crystalline alkaloid, melting at 200° (uncorr.), insoluble in water, sparingly soluble in light petroleum, more readily so in ether, chloroform, or absolute alcohol, and very soluble in pyridine. The freshly precipitated amorphous base is very soluble in ether or chloroform. Pukateine is precipitated from its solution by a slight excess of acetic acid, and by iodine in potassium iodide, picric acid, auric chloride, platinic chloride, bromine water, ammonia, Mayer's reagent, disodium hydrogen phosphate, and phosphomolybdic acid. It is soluble in alkali hydroxide solutions, and is reprecipitated on passing a current of carbon dioxide through the solution. In both hydrochloric acid and alkali solutions, hydrolysis of pukateine salts has been observed, the crystalline base being precipitated on dilution and heating. Five preparations were analysed:

I. Recrystallised from alcohol, dried at 100°; m. p. 200°:

0·0741 gave 0·1964 CO_2 and 0·0411 H_2O. C = 72·27; H = 6·17.

2. Recrystallised from alcohol; m. p. 200°:

0·1259 gave 0·3319 CO_2 and 0·0676 H_2O. C=71·89; H=5·97.

3. Precipitated in a crystalline state by addition of sodium carbonate to the solution in dilute acetic acid:

0·0776 gave 0·20545 CO_2 and 0·0428 H_2O. C=72·19; H=6·14.

4. Recrystallised from absolute alcohol:

0·2588 gave 10·8 c.c. N_2 at 22° and 764 mm. N=4·80.

5. 0·2181 „ 9·6 c.c. N_2 „ 20° „ 769 mm. N=5·09.

$C_{17}H_{17}O_3N$ requires C=72·08; H=6·01; N=4·95 per cent.

Molecular-weight Determinations.

0·1604, in 7·12 of phenol, gave $\Delta t = -0·6°$. M.W.=277.

0·656 in 16·5 „ „ $\Delta t = -0·925°$. M.W.=317.

$C_{17}H_{17}O_3N$ requires M.W.=283.

Solubilities.

100 parts of	boiling alcohol	dissolve	4·17	parts of pukateine.
100 ,,	alcohol at 17·5°	,,	1·10	,, ,,
100 ,,	boiling ether	,,	0·84	,, ,,
100 ,,	ether at 17°	,,	0·62	,, ,,

Optical Activity.—An alcoholic solution containing 0·6 gram in 100 c.c. gave a rotation of no less than −2·64° in a 2-dcm. tube, whence α_D^{15} −220°.

Colour Reactions.—If a solution of potassium dichromate in concentrated sulphuric acid, prepared as for the strychnine reaction, is brought into contact in not too great excess with a few crystals of pukateine, a persistent purple coloration is produced. If excess of the reagent is applied, a green colour merely results. The colour which the reagent gives with strychnine cannot be confused with that given with pukateine. The former is a bright violet, quickly changing to purple, and finally to a bright red. At one stage the purple colour of the strychnine reaction closely resembles that of pukateine, but the ephemeral nature of the one precludes confusion with the other. Concentrated nitric acid dissolves pukateine, with the formation of a dark red colour closely resembling that given by morphine.

Concentrated sulphuric acid alone produces a dull purple colour with pukateine if heat is gently applied.

If one drop of a very dilute solution of potassium nitrite is added to a solution of pukateine in slight excess of sulphuric acid, a dark reddish-brown or green solution is developed. The base remains unchanged in dilute sulphuric acid solutions.

If a solution of pukateine in sodium hydroxide is kept in an open test-tube for a few hours, the solution becomes green, and on acidifying with hydrochloric acid and extracting with ether, a purple, ethereal layer results. (The experiment was repeated with the purest pukateine, recrystallised from sodium hydroxide solution.) The amount of colouring matter formed was too small to examine.

On heating small quantities of pukateine with soda-lime or zinc dust, no odour of quinoline or pyridine could be detected.

No methoxy-groups could be detected when the substance was examined by Zeisel's method.

Nitric acid in cold glacial acetic acid solution gives rise to a highly acidic nitro-derivative, which dissolves in alkalis, yielding an orange-red solution.

Concentrated sulphuric acid dissolves pukateine slowly when they are triturated together in a mortar, and on diluting the syrupy solution with water an insoluble, amorphous, white compound containing nitrogen is formed.

Hydrochloric acid, heated with one-fifth of its weight of pukateine in a sealed tube at 110°, completely converts the pukateine into a glassy mass, insoluble in ordinary solvents.

With water in a sealed tube at 140°, no similar effect is produced.

Salts of Pukateine.

(*a*) *Salts with Acids.*—The *hydrochloride*, $C_{17}H_{17}O_3N,HCl$, is easily prepared by dissolving the base in hot concentrated hydrochloric acid, and rapidly filtering. On cooling the filtrate, a crystalline, hydrochloride separates out. This is collected and dried on a porous plate. The anhydrous salt is obtained by drying at a temperature of 50° to 60° under diminished pressure:

0·5751 neutralised 18·02 c.c. $N/10$-NaOH. HCl = 11·37.
0·1842 ,, 5·80 c.c. $N/10$-NaOH. HCl = 11·50.
0·1651 gave 0·075 AgCl. Cl = 11·22.

$C_{17}H_{17}O_3N,HCl$ requires HCl = 11·42; Cl = 11·11 per cent.

The *platinichloride* was prepared by the addition of platinic chloride to the solution of pukateine hydrochloride in water. It was washed with hot water, and dried in a desiccator under diminished pressure:

0·148 salt gave 0·0298 Pt. Pt = 20·1.

$(C_{17}H_{17}O_3N)_2,H_2PtCl_6$ requires Pt = 20·0 per cent.

(*b*) *Salts with Metals: Potassium and Sodium Salts.*—Pukateine dissolves in solutions of potassium or sodium hydroxides, but if the solution is diluted and boiled, the alkaloid is reprecipitated in characteristic prisms, melting at 200°. The addition of solid alkali hydroxide to the hot concentrated solution eventually causes metallic salts to be precipitated, and the solution, on cooling, sets to a magma of hair-like crystals. After collection on an asbestos filter and drying on a porous tile over sulphuric acid, the crystals gave analytical results agreeing with the formula $C_{17}H_{16}MO_3N$ (M = Na or K). The salts blacken without melting at a temperature below 250°.

For analysis, the salts were dissolved in dilute alcohol, and titrated with phenolphthalein.

Potassium Salt.

0·1994 neutralised 6·1 c.c. *N*/10-HCl. K = 11·9.

$C_{17}H_{16}O_3NK$ requires K = 12·15 per cent.

Sodium Salt.

0·0919 neutralised 2·95 c.c. *N*/10-HCl. Na = 7·4.

0·1015 gave 0·0235 Na_2SO_4. Na = 7·48.

$C_{17}H_{16}O_3NNa$ requires Na = 7·54 per cent.

Professor John Malcolm, of Dunedin, is investigating the pharmacology of the alkaloids of the pukatea, and furnishes the following preliminary note.

"Pukateine itself is apparently inactive, due probably to its insolubility. The hydrochloride is very soluble, and shows some of the typical actions of the alkaloids in general.

"Like strychnine, although in relatively much larger doses (0·25 gram per kilo.), it has a convulsant action on the nerve cells of the spinal cord. In the rabbit the convulsions resemble closely those of strychnine poisoning, but in the frog the effect of the drug on the peripheral neuro-muscular apparatus modifies the result, for, although the spasms are easily set up and begin by an intense general contraction of all the muscles of the body, relaxation follows almost immediately. An isolated nerve muscle preparation from such a frog cannot be tetanised by a succession of stimuli—the contraction begins well, but ceases very soon, although the stimulation continues.

"This is probably allied to the general action of alkaloids in paralysing the motor nerve endings in muscle, or it may be regarded as a fatigue phenomenon.

"Apart from such alkaloidal effects, pukateine salts have not been found to possess any marked pharmacological actions. On intravenous injection, the blood pressure falls slightly, the heart beats slowly and forcibly, and death results from respiratory failure, sometimes with great suddenness.

"When the alkaloid is rubbed on the tongue, some localised numbness is felt, and in frogs under the influence of the drug there may be no reflex response from some areas of the skin, whilst other areas give reflexes, but this effect appears late, and is probably due to an action on the nerve cells of the spinal cord."

Laureline.

The preparation of crude laureline sulphate has already been described. To purify it, the salt was dissolved in hot water, and potassium chromate solution added. On cooling, the chromate was precipitated in yellow, amorphous flocks. The chromate was dissolved in hot sodium hydroxide, cooled, acidified with hydrochloric acid, and the base precipitated by sodium carbonate. This was dissolved in ether, and the ether evaporated. Dilute sulphuric acid converted the syrupy residue from the ether into yellowish-white crystals, which slowly become pink. The sulphate crystallises well from dilute sulphuric acid, the mother liquor turning brown on keeping. The sulphate melts and decomposes at about 105°. Laureline salts give the usual reactions with alkaloid reagents, and have a bitter taste. Four preparations were analysed:

Laureline sulphate.—Containing water of crystallisation:

1. The substance was heated to 90° under diminished pressure.
   0·2455 lost 0·0362. $H_2O=14·74$.
2. 0·0839 lost 0·0125. $H_2O=14·90$.
3. 0·3664 ,, 0·0554. $H_2O=15·12$.

$(C_{19}H_{21}O_3N)_2,H_2SO_4,7H_2O$ requires $H_2O=14·89$ per cent.

1. Dried at 90° under diminished pressure:

0·2151 gave 6·4 c.c. N_2 at 20° and 760 mm. N=3·4.

2. Regenerated from the chromate and recrystallised from acidified water; dried at 90° under diminished pressure:

0·12 gave 0·2795 CO_2 and 0·067 H_2O. C=63·52; H=6·22.

3. Recrystallised from acidified water; dried at 90° under diminished pressure:

0·1702 gave 0·3984 CO_2 and 0·1004 H_2O. C=63·84; H=6·56.
0·2127 ,, 0·07 $BaSO_4$. S=4·52.

4. 0·202 ,, 6·9 c.c. N_2 at 17° and 760 mm. N=3·96.
0·1418 ,, 0·0513 $BaSO_4$. S=4·97.

$(C_{19}H_{21}O_3N)_2,H_2SO_4$ requires C=63·33; H=6·11; N=3·90; S=4·44 per cent.

Laureline Hydrochloride.—This salt is easily prepared by dissolving the sulphate in boiling water and adding excess of hydrochloric acid. On cooling, the hydrochloride is precipitated in fine crystals. Two preparations were analysed:

1. Air-dried on porous tile:

   0·4662 neutralised 5·44 c.c. *N*/10-NaOH. Cl = 10·39.

   0·2791 gave 0·1157 AgCl. Cl = 10·24.

2. 0·1019 gave 0·0426 AgCl. Cl = 10·32.

$C_{19}H_{21}O_3N,HCl$ requires Cl = 10·21 per cent.

Laureline Nitrate.

0·099 gave 7·2 c.c. N_2 and 22° and 744 mm. N = 8·03.

$C_{19}H_{21}O_3N,HNO_3$ requires N = 7·65 per cent.

Most of the salts of laureline are very soluble in boiling water, but sparingly so in cold water. Several different salts may therefore be made with the same material without much loss. On precipitating the sulphuric acid from the solution of the sulphate with barium chloride in boiling acid solution, laureline hydrochloride separates from the filtrate on cooling. Similarly, on precipitating the chloride in boiling nitric acid solution with silver nitrate, the white, crystalline nitrate is precipitated in the filtrate as it cools, subsequently becoming of a brick-red colour.

Laurepukine.

The crude, amorphous, dark brown alkaloid, the preparation of which has already been described, was dissolved in dilute acetic acid, and fractionally precipitated by the addition of sodium carbonate. By this means the alkaloid was obtained as an almost colourless powder, which dissolved readily in acids, but from which no crystalline salts were obtained. When prepared in this way, the substance is a yellowish-white powder, which melts indefinitely at about 100° to a resinous mass. Analyses and molecular-weight determinations agree approximately with the formula $C_{16}H_{19}O_3N$:

Found, C = 70·3; H = 6·6; N = 4·9. M.W. = 315.

$C_{16}H_{19}O_3N$ requires C = 70·33; H = 6·9; N = 5·14 per cent. M.W. = 272.

In view of the doubtful purity of the substance, great importance must not be attached to these figures. Laurepukine dissolves in benzene, and the solution, on keeping, slowly develops a purple colour.

In conclusion, I must express my thanks to Professor Easterfield for the interest he has taken in this research (which is being continued), and for having defrayed a portion of the cost of the investigation from a grant made to him by the Royal Society of London for researches on the poisonous plants of New Zealand.

VICTORIA COLLEGE,
WELLINGTON, N.Z.

CXXVIII.—*The Action of Alkalis on Certain Derivatives of Coumarin.*

By Arthur Clayton, B.Sc., A.R.C.S.

The two most important reactions between alkalis and the aromatic lactones of the coumarin series are the formation of the sodium salt of a coumarinic acid simply by dissolving the coumarin in aqueous sodium hydroxide, and the production of the corresponding *o*-coumaric acid by the prolonged action of alcoholic solutions of the alkali. The former change is of special interest, because the constitution of coumarinic acid must still be regarded as uncertain, and because it has not yet been found possible to isolate the acid from its salts. The only derivative of coumarinic acid which has heretofore been obtained in the free state is 8-nitrocoumarinic acid, obtained by dissolving 8-nitrocoumarin in aqueous sodium hydroxide, and subsequently acidifying the solution at a low temperature (Miller and Kinkelin, *Ber.*, 1889, **22**, 1706). This acid is very unstable, being resolved into 8-nitrocoumarin and water when warmed with alcohol or water.

In the present communication an account is given of a general investigation of the action of alkalis on substituted coumarins, and more particularly in connexion with the various nitrocoumarins. In order to obtain nitrocoumarins with the nitro-groups in different positions, several of the alkylated coumarins previously prepared by the author (Trans., 1908, **93**, 2016) were nitrated, the entrant groups being forced into desired positions by the alkyl groups already present. In addition to the nitrocoumarins, other coumarins with different substituents were examined, and incidentally it became possible to trace the influence of alkyl groups. The orientation of many of the compounds obtained during the present investigation presented considerable difficulty, owing to the paucity of knowledge of the derivatives of the homologues of coumarin.

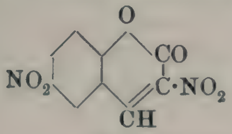
The Nitro-derivatives of Coumarin.

The only nitrocoumarins described in the literature are 6-nitrocoumarin, obtained by the direct nitration of coumarin (Delalande, *Annalen*, 1843, **45**, 337), and 8-nitrocoumarin, the product obtained by heating together 3-nitrosalicylaldehyde, sodium acetate, and acetic anhydride (Miller and Kinkelin, *loc. cit.*).

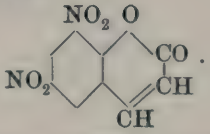
Since 8-nitrocoumarin forms an unstable coumarinic acid when its alkaline solution is cautiously acidified, and this formation appears to depend on the presence and position of the nitro-group, it appeared probable that 6: 8-dinitrocoumarin would yield a more stable coumarinic acid when similarly treated. With the object of preparing this acid for future investigation, coumarin was treated with nitric acid under various conditions. Coumarin was found to resist strongly the introduction of more than one nitro-group (p. 1397), but this resistance diminishes very appreciably with the addition of alkyl groups to the molecule. A dinitrocoumarin was finally obtained, melting at 180—181°.

Orientation of the Dinitrocoumarin (m. p. 180—181°) *obtained by Nitrating Coumarin.*

One of the nitro-groups was known to occupy position 6,* as the dinitrocoumarin could also be prepared by further nitrating 6-nitrocoumarin. The second nitro-group was expected to enter position 8. An attempt was therefore made to prepare the dinitrocoumarin by nitrating 8-nitrocoumarin, but the dinitrocoumarin obtained by this operation melted at 159—160°. The compound melting at 180—181° was therefore oxidised with alkaline potassium permanganate, and yielded 5-nitrosalicylic acid.* The dinitration of coumarin therefore furnishes a product containing one nitro-group in position 6, and the other in the lactonic ring. The exact position of the lactonic nitro-group is shown by the action of sodium hydroxide to be position 3 (see below). The dinitrocoumarin (m. p. 180—181°) produced by the direct nitration of coumarin is therefore 3: 6-*dinitrocoumarin* (formula I):



(I.)



(II.)

The dinitrocoumarin (m. p. 159—160°) produced by nitrating 8-nitrocoumarin is shown by its action with sodium hydroxide (p. 1390) not to contain a nitro-group in the lactonic ring, and since the nitro-group always enters position 6 if this be open, the compound must be 6: 8-*dinitrocoumarin* (formula II).

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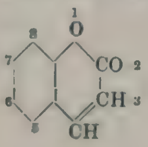
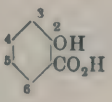
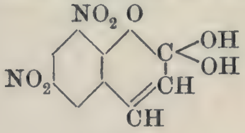
* The method of numbering the positions in the coumarin and salicylic acid molecules is indicated in the following formulæ :



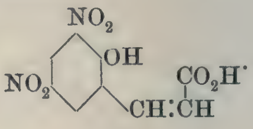


The Action of Alkalis on the Dinitrocoumarins.

6 : 8-*Dinitrocoumarin.*—This compound dissolves in weak aqueous sodium hydroxide to a deep orange-red liquid, which, when acidified with cold dilute hydrochloric acid, furnishes a yellow precipitate, melting at about 155°, with a copious evolution of vapour. This substance was shown to be different from 6 : 8-dinitrocoumarin by the method of mixed melting points. The new compound was also much more soluble in alcohol and water than 6 : 8-dinitrocoumarin, but was rapidly changed into the latter compound when heated with either of these solvents. These facts indicate that the new substance is 6 : 8-*dinitrocoumarinic acid*, and this conclusion is confirmed by the very similar properties possessed by 8-nitrocoumarinic acid (Miller and Kinkelin, *loc. cit.*). The formula of the new coumarinic acid is therefore III or IV, according as to whether the hypothetical coumarinic acid is regarded as a derivative of carbonic acid or a *cis*-isomeride of *o*-coumaric acid:



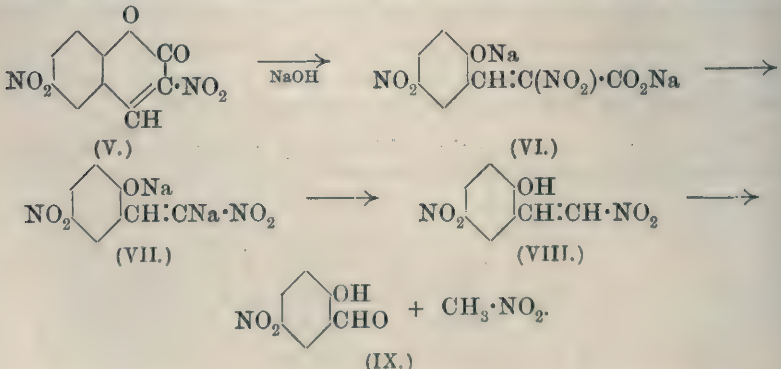
(III.)



(IV.)

3 : 6-*Dinitrocoumarin.*—When warmed with aqueous sodium hydroxide, or preferably concentrated ammonia solution, 3 : 6-dinitrocoumarin dissolves to a deep orange-red liquid, which, on subsequent acidification with hydrochloric acid, yields 5-nitrosalicylaldehyde. This remarkably easy rupture of the lactonic ring was subsequently found to be a property conferred on all coumarins by the presence of a nitro-group in position 3.

In order to trace the course of the above reaction, the sodium salt produced by dissolving 3 : 6-dinitrocoumarin in sodium



hydroxide was isolated, and found to be the sodium salt of 5-nitrosalicylaldehyde. No other intermediate product was obtained, but in the case of a 4-methyl substituted 3 : 6-dinitrocoumarin, the styrene derivatives corresponding with formulæ VII and VIII were isolated (see p. 1392). The reaction resulting in the formation of 5-nitrosalicylaldehyde is thus shown to follow the course outlined by formulæ V—IX (p. 1390).

The whole of the degradation takes place before the addition of the acid, the latter merely liberating the aldehyde from its salt.

It is worthy of note that when benzaldehyde and nitromethane are heated together, ω-nitrostyrene is produced (Priebs, *Annalen*, 1884, **225**, 321).

The Nitro-derivatives of 7-Methylcoumarin and 4 : 7-Dimethylcoumarin.

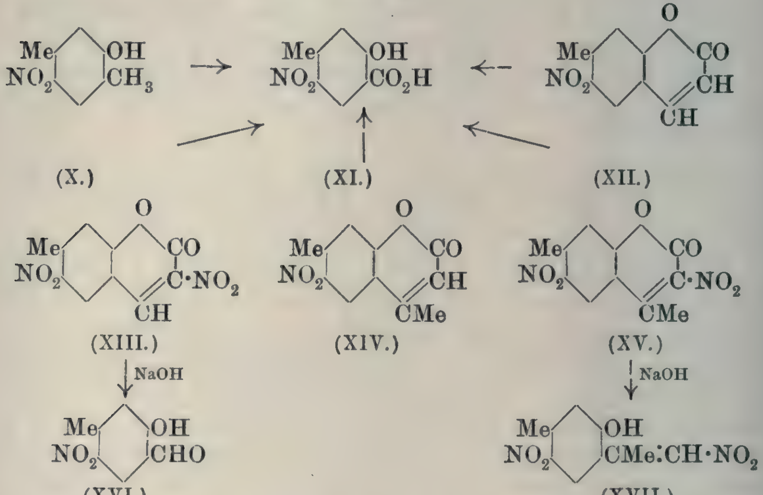
The nitro-derivatives of 7-methylcoumarin and 4 : 7-dimethylcoumarin and the dinitro-derivative of 7-methylcoumarin were prepared similarly to the corresponding compounds of coumarin itself. The dinitration of 4 : 7-dimethylcoumarin proceeded readily at the ordinary temperature, the presence of a methyl group in position 4 appearing very greatly to facilitate the entry of the second nitro-group. The orientation of the nitro-derivatives of this series was accomplished in the manner outlined by formulæ X—XVII. 4-Nitro-*p*-xylenol (X) was oxidised by alkaline potassium permanganate to 5-*nitro-4-methylsalicylic acid* (XI). This acid was then produced by the oxidation of each of the four nitro-derivatives under examination. The nitro-derivatives of 7-methylcoumarin and 4 : 7-dimethylcoumarin are thus shown to be 6-*nitro-7-methylcoumarin* (XII) and 6-nitro-4 : 7-dimethylcoumarin (XIV) respectively. The corresponding dinitro-derivatives are also shown to contain a nitro-group in position 6, and a second in the lactonic ring. The exact position of the second nitro-group is proved by the action of sodium hydroxide (see below).

The Action of Alkalis on the Products of Nitration of 7-Methylcoumarin and 4 : 7-Dimethylcoumarin.

6-Nitro-7-methylcoumarin and 6-nitro-4 : 7-dimethylcoumarin dissolve in aqueous sodium hydroxide, the former more readily than the latter, forming orange solutions, which, however, when carefully acidified, only regenerate the original nitro-compounds.

The dinitro-derivative of 7-methylcoumarin forms with aqueous sodium hydroxide an orange-red solution, which, when acidified, yields 5-*nitro-4-methylsalicylaldehyde* (XVI), of which the oxime and phenylhydrazone were prepared. The above dinitro-derivative is therefore shown to be 3 : 6-*dinitro-7-methylcoumarin* (XIII).

The dinitro-derivative of 4 : 7-dimethylcoumarin dissolves in aqueous sodium hydroxide to an orange liquid, which, when carefully acidified, yields ω-5-*dinitro-2-hydroxy-α-4-dimethylstyrene* (XVII). The parent dinitro-derivative is thus shown to be 3 : 6-*dinitro*-4 : 7-*dimethylcoumarin* (XV):

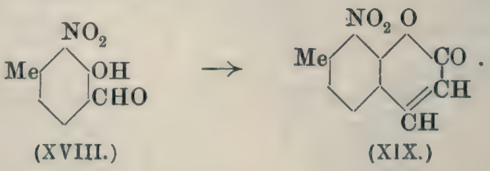


(X.) (XI.) (XII.)

(XIII.) (XIV.) (XV.)

(XVI.) (XVII.)

Before the above orientations had been worked out, the constitution of 6-nitro-7-methylcoumarin had been indicated by nitrating 4-methylsalicylaldehyde and heating the resulting 3-*nitro*-4-*methylsalicylaldehyde* (XVIII) with sodium acetate and acetic anhydride, thereby obtaining 8-*nitro*-7-*methylcoumarin* (XIX). The latter compound was then shown to be different from the nitration product of 7-methylcoumarin, thus indicating this nitration product to be 6-nitro-7-methylcoumarin :



(XVIII.) (XIX.)

The Nitration Products of 6 : 7-*Dimethylcoumarin and* 4 : 6 : 7-*Trimethylcoumarin.*

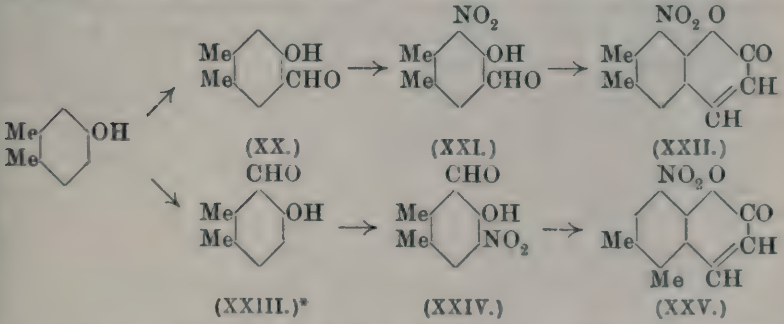
6 : 7-Dimethylcoumarin yields mono-, di-, and tri-nitro-derivatives at the ordinary temperature. 4 : 6 : 7-Trimethylcoumarin was nitrated with even greater ease, an extraordinary readiness to form

the trinitro-derivative being manifested. So great was this tendency that it was not found possible to prepare the dinitro-derivative. From these and the foregoing results there can be no doubt that the difficulty of obtaining the higher nitration products of coumarin is due to the general acidity conferred on the molecule by the lactonic ring, and that the introduction of methyl groups gradually weakens this acidity and makes the molecule more susceptible to the action of nitric acid. A methyl group in the lactonic ring is seen to be specially efficacious in this respect.

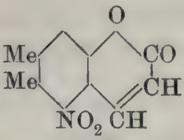
The orientation of the nitration products of this series could not be effected by methods of oxidation. The following process was therefore adopted for the orientation of the nitro-derivative of 6 : 7-dimethylcoumarin.

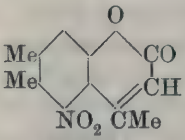
Since this compound does not behave towards sodium hydroxide in the manner characteristic of coumarins with a nitro-group in the lactonic ring, the nitro-group must occupy position 5 or 8.

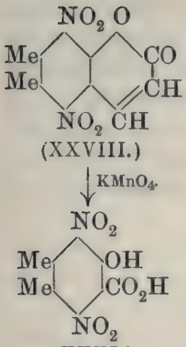
o-4-Xylenol was submitted to the Tiemann reaction, and yielded a product which, when crystallised from light petroleum, separated into long, spiky needles and pearly flakes. These crystals were separated mechanically, and separately recrystallised from light petroleum. Both compounds melted at 71—72°, and formed compounds with sodium hydrogen sulphite, but were shown to be different by the method of mixed melting points. The oxidation of the flaky compound by fused potassium hydroxide yielded 4 : 5-dimethylsalicylic acid, thus proving the aldehyde crystallising in flakes to be 4 : 5-*dimethylsalicylaldehyde* (XX). The latter compound, on nitration, yields 3-*nitro*-4 : 5-*dimethylsalicylaldehyde* (XXI), which was converted by the Perkin reaction into 8-*nitro*-



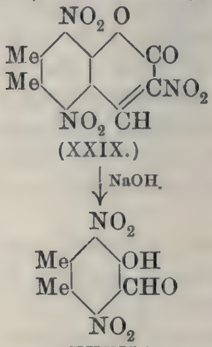
[*] In order to complete the study of this branch of the coumarins, the second compound (acicular crystals) obtained from *o*-4-xylenol was first shown to be 5 : 6-*dimethylsalicylaldehyde* (XXIII) by preparing its sodium hydrogen sulphite compound, and by oxidising it to 5 : 6-*dimethylsalicylic acid*. The aldehyde was then nitrated, yielding 3-*nitro*-5 : 6-*dimethylsalicylaldehyde* (XXIV), which was converted by the Perkin reaction into 8-*nitro*-4 : 5-*dimethylcoumarin* (XXV).


(XXVI.)

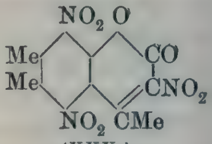

(XXVII.)


(XXVIII.)

(XXXI.)


(XXIX.)

(XXXII.)


(XXX.)

6 : 7-*dimethylcoumarin* (XXII). The latter compound proved to be different from the substance obtained by nitrating 6 : 7-dimethylcoumarin, therefore this nitration product must be 5-*nitro*-6 : 7-*dimethylcoumarin* (XXVI), and from analogy the nitro-derivative of 4 : 6 : 7-trimethylcoumarin is 5-*nitro*-4 : 6 : 7-*trimethylcoumarin* (XXVII).

The orientation of the dinitro-derivative of 6 : 7-dimethylcoumarin was effected by oxidation with alkaline potassium permanganate, this operation yielding 3 : 6-*dinitro*-4 : 5-*dimethylsalicylic acid* (XXXI), thus showing the compound under examination to be 5 : 8-*dinitro*-6 : 7-*dimethylcoumarin* (XXVIII).

The trinitro-derivatives of 6 : 7-dimethylcoumarin and 4 : 6 : 7-trimethylcoumarin must contain a nitro-group in the lactonic ring, and are therefore 3 : 5 : 8-trinitro-6 : 7-dimethylcoumarin (XXIX) and 3 : 5 : 8-*trinitro*-4 : 6 : 7-*trimethylcoumarin* (XXX). The behaviour of these compounds towards sodium hydroxide (see below) confirms this view.

The Action of Alkalis on the Products of Nitration of 6 : 7-Dimethylcoumarin and 4 : 6 : 7-Trimethylcoumarin.

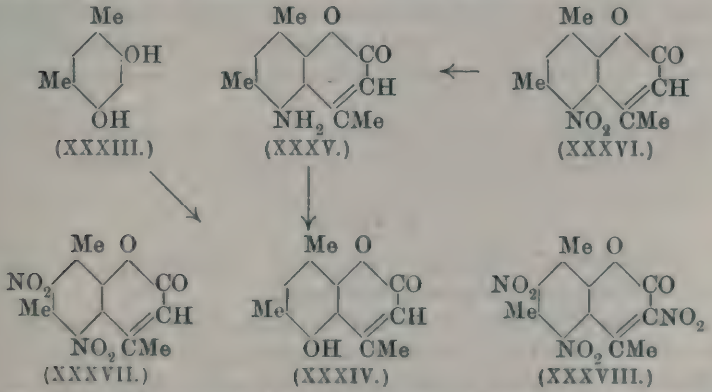
5-Nitro-6 : 7-dimethylcoumarin and 5-nitro-4 : 6 : 7-trimethylcoumarin dissolve slightly in aqueous sodium hydroxide, the latter less readily than the former, yielding orange-yellow solutions, from which acidification regenerates the nitro-derivatives. 5 : 8-Dinitro-6 : 7-dimethylcoumarin dissolves readily in aqueous sodium hydroxide to an orange-red solution, which, on acidification at −5°, yields a compound melting at about 168° with a copious evolution of vapour. On recrystallising this compound from alcohol, or even keeping it in the dry state for a few hours, 5 : 8-dinitro-6 : 7-dimethylcoumarin is regenerated. The precipitate obtained as above is probably an extremely unstable coumarinic acid.

3 : 5 : 8-Trinitro-6 : 7-dimethylcoumarin dissolves readily in aqueous sodium hydroxide to an orange-red solution, which, when acidified, yields 3 : 6-dinitro-4 : 5-dimethylsalicylaldehyde (XXXII). The course of the reaction is therefore strictly analogous with that outlined by formulæ V—IX.

3 : 5 : 8-Trinitro-4 : 6 : 7-trimethylcoumarin dissolves in aqueous sodium hydroxide to an orange-red solution, but no definite compound was isolated from the sticky material produced on acidification.

The Nitro-derivatives of 4 : 6 : 8-*Trimethylcoumarin.*

4 : 6 : 8-Trimethylcoumarin yields mono-, di-, and tri-nitro-derivatives at the ordinary temperature. The orientation of these nitro-derivatives could not be carried out by methods of oxidation. The constitution of the nitro-derivative of 4 : 6 : 8-trimethylcoumarin was accomplished in the manner indicated by formulæ XXXIII—XXXVI. 4 : 6-Dimethylresorcinol (XXXIII) was condensed with ethyl acetoacetate, yielding 5-*hydroxy*-4 : 6 : 8-*trimethylcoumarin* (XXXIV). The latter compound was then prepared from the nitro-derivative of 4 : 6 : 8-trimethylcoumarin by reducing it to the corresponding amine, and converting this compound through its diazonium chloride into 5-hydroxy-4 : 6 : 8-trimethylcoumarin. The nitro-derivative of 4 : 6 : 8-trimethylcoumarin is therefore 5-*nitro*-4 : 6 : 8-*trimethylcoumarin* (XXXVI), and its reduction product, 5-*amino*-4 : 6 : 8-*trimethylcoumarin* (XXXV):

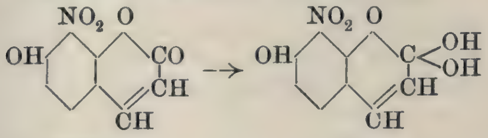


The dinitro-derivative of 4 : 6 : 8-trimethylcoumarin is practically unaffected by aqueous sodium hydroxide; hence it does not contain a nitro-group in the lactonic ring, and must be 5 : 7-*dinitro*-4 : 6 : 8-*trimethylcoumarin* (XXXVI). The trinitro-derivative can only be 3 : 5 : 7-*trinitro*-4 : 6 : 8-*trimethylcoumarin* (XXXVIII).

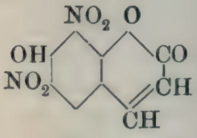
5-Nitro-4 : 6 : 8-trimethylcoumarin and 5 : 7-dinitro-4 : 6 : 8-trimethylcoumarin remain practically unattacked when boiled with aqueous sodium hydroxide. 3 : 5 : 7-Trinitro-4 : 6 : 8-trimethylcoumarin dissolves in this reagent to an orange-red liquid, which, however, yields no crystalline product on acidification.

The Nitro-derivatives of 7-Hydroxycoumarin (Umbelliferone).

The only nitro-derivative of umbelliferone mentioned in the literature is trinitroumbelliferone (Posen, *Ber.*, 1881, **14**, 2747), which does not appear to have been orientated, but which is described as being decomposed by sodium hydroxide. It is therefore very possibly 3 : 6 : 8-trinitroumbelliferone. The author of the present communication prepared nitro- and dinitro-umbelliferone, the action proceeding at the ordinary temperature. From analogy to the corresponding nitro-derivatives of 4-methylumbelliferone, the compounds in question are 8-nitroumbelliferone (XXXIX) and 6 : 8-*dinitroumbelliferone* (XLI):



(XXXIX.) (XL.)



(XLI.)

Aqueous sodium hydroxide dissolves 8-nitroumbelliferone (yellow) to a red liquid, furnishing, on acidification, a scarlet precipitate of 8-*nitrocoumarinic acid*, which, if the carbonic acid formula be adopted, has the constitution indicated by (XL). This coumarinic acid is the most stable of those yet discovered, and may easily be crystallised from dry ether. When heated, however, it slowly reverts to 8-nitroumbelliferone.

6 : 8-Dinitroumbelliferone dissolves easily in aqueous sodium hydroxide, but is regenerated when the solution is acidified.

Summary.

1. A number of nitration products of coumarin and its homologues have been prepared and orientated.

2. Position 3 in the lactonic ring has been shown to be peculiarly susceptible to the action of nitric acid, the nitro-group often entering this position when other positions are open in the benzenoid ring.

3. Nitrocoumarins containing a nitro-group in position 8, and unsubstituted in the lactonic ring, show a tendency to form free coumarinic acids. This tendency is decreased by the presence of alkyl groups in the molecule.

4. Several coumarinic acids have been prepared. They are all more or less unstable.

5. Coumarins containing a nitro-group in position 3, and not substituted in position 4, yield aldehydes when treated with sodium hydroxide. This reaction has been investigated in several typical cases, and forms a new method for preparing aromatic hydroxy-aldehydes.

6. Coumarins containing a nitro-group in position 3, and an alkyl group in position 4, react with sodium hydroxide to form the corresponding ω-nitrostyrene.

EXPERIMENTAL.

I.—*The Nitration of Coumarin and its Homologues.*

The Nitro-derivatives of Coumarin.

3 : 6-*Dinitrocoumarin.*—6-Nitrocoumarin (4 grams) was dissolved in concentrated sulphuric acid (20 c.c.), and treated with a nitrating mixture * at a temperature below 5°. The resulting liquid, after remaining at the ordinary temperature for one hour, was gradually heated to 100°, and maintained at this temperature for twenty minutes. The cooled solution was then poured on ice, and the solid which separated was collected. After two or three crystallisations from glacial acetic acid, yellow needles were obtained, melting at 180—181°:

0·1227 gave 0·2063 CO_2 and 0·0203 H_2O. $C=45·85$; $H=1·84$.

0·1051 „ 10·8 c.c. N_2 at 19° and 756 mm. $N=11·81$.

$C_9H_4O_6N_2$ requires $C=45·76$; $H=1·69$; $N=11·86$ per cent.

6 : 8-*Dinitrocoumarin*, prepared by nitrating 8-nitrocoumarin in the foregoing manner, crystallised from glacial acetic acid in yellow needles, melting at 159—160°:

0·0958 gave 0·1613 CO_2 and 0·0173 H_2O. $C=45·93$; $H=2·01$.

0·1068 „ 11·4 c.c. N_2 at 21° and 750 mm. $N=11·99$.

$C_9H_4O_6N_2$ requires $C=45·76$; $H=1·69$; $N=11·86$ per cent.

The Nitro-derivatives of 7-Methylcoumarin and 4 : 7-*Dimethylcoumarin.*

6-*Nitro-7-methylcoumarin.*—7-Methylcoumarin (4 grams) was dissolved in concentrated sulphuric acid (20 c.c.), and treated at 0°

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* The "nitrating mixture" used throughout these experiments consisted of 1 volume of nitric acid (D 1·4) and 3 volumes of concentrated sulphuric acid.

with the nitrating mixture (8 c.c.). The liquid was kept at the ordinary temperature for one hour, and then poured on ice, when a white solid separated, which crystallised from glacial acetic acid in white needles, melting at 223—224°:

0·1939 gave 0·4143 CO_2 and 0·0625 H_2O. C = 58·27; H = 3·58.
0·2587 „ 15·2 c.c. N_2 at 23° and 748 mm. N = 6·52.
$C_{10}H_7O_4N$ requires C = 58·53; H = 3·41; N = 6·83 per cent.

3 : 6-*Dinitro-7-methylcoumarin.* — 6-Nitro-7-methylcoumarin (3 grams), dissolved in concentrated sulphuric acid (10 c.c.), was treated at 0° with the nitrating mixture (5 c.c.). The solution was kept at the ordinary temperature for one hour, and then gradually heated to 100°, at which temperature it was maintained for twenty minutes. The cooled liquid was poured on ice, and yielded a product which crystallised from glacial acetic acid in yellow needles, melting at 164—165°:

0·2316 gave 0·4097 CO_2 and 0·0545 H_2O. C = 48·24; H = 2·61.
0·2093 „ 21·4 c.c. N_2 at 24° and 753 mm. N = 11·35.
$C_{10}H_6O_6N_2$ requires C = 48·00; H = 2·40; N = 11·20 per cent.

6-*Nitro*-4 : 7-*dimethylcoumarin.* — 4 : 7 - Dimethylcoumarin (4 grams), dissolved in concentrated sulphuric acid (20 c.c.), was treated at 0° with the nitrating mixture (7·5 c.c.). After remaining at the ordinary temperature for one hour, the liquid was poured on ice, when a white solid separated, which crystallised from glacial acetic acid in colourless needles, melting at 252—253°:

0·1804 gave 0·4000 CO_2 and 0·0718 H_2O. C = 60·48; H = 4·42.
0·1944 „ 10·4 c.c. N_2 at 15° and 773 mm. N = 6·37.
$C_{11}H_9O_4N$ requires C = 60·27; H = 4·11; N = 6·39 per cent.

3 : 6-*Dinitro*-4 : 7-*dimethylcoumarin.*—4 : 7-Dimethylcoumarin (4 grams) was dissolved in concentrated sulphuric acid (20 c.c.), and slowly treated at 0° with the nitrating mixture (12 c.c.). The liquid was kept overnight, and then poured on ice; the white precipitate crystallised from glacial acetic acid in colourless needles, melting and decomposing at about 235°:

0·1353 gave 0·2494 CO_2 and 0·0400 H_2O. C = 50·28; H = 3·28.
0·2056 „ 18·6 c.c. N_2 at 20° and 764 mm. N = 10·40.
$C_{11}H_8O_6N_2$ requires C = 50·00; H = 3·03; N = 10·61 per cent.

The Nitro-derivatives of 6 : 7-*Dimethylcoumarin and* 4 : 6 : 7-*Trimethylcoumarin.*

8-*Nitro*-6 : 7-*dimethylcoumarin.* — 6 : 7-*Dimethylcoumarin* (3·4 grams), dissolved in concentrated sulphuric acid (30 c.c.), was treated at 0° with the nitrating mixture (7·5 c.c.), and the resulting liquid kept at the ordinary temperature for one hour. The solution was then poured on ice, when a solid was obtained which, after crystallisation from glacial acetic acid, formed white needles, melting at 210—211°:

0·1130 gave 0·2491 CO_2 and 0·0457 H_2O. C = 60·12; H = 4·49.
0·3000 „ 16·9 c.c. N_2 at 24° and 747 mm. N = 6·21.
$C_{11}H_9O_4N$ requires C = 60·27; H = 4·11; N = 6·39 per cent.

5 : 8-*Dinitro*-6 : 7-*dimethylcoumarin*.—6 : 7-Dimethylcoumarin (2·4 grams) was dissolved in concentrated sulphuric acid (25 c.c.), treated at 0° with the nitrating mixture (8·8 c.c.), and the liquid kept overnight at the ordinary temperature. It was then poured on ice, when a solid was obtained which crystallised from glacial acetic acid in pale yellow needles, melting at 175—176°. The yellow colour was completely removed by boiling with 50 per cent. acetic acid and a little animal charcoal. The substance possesses a peculiar and characteristic odour:

0·1347 gave 0·2457 CO_2 and 0·0415 H_2O. C = 49·74; H = 3·43.
0·0945 „ 9·1 c.c. N_2 at 20° and 764 mm. N = 11·07.
$C_{11}H_8O_6N_2$ requires C = 50·00; H = 3·03; N = 10·61 per cent.

3 : 5 : 8-*Trinitro*-6 : 7-*dimethylcoumarin*.—6 : 7-Dimethylcoumarin (5 grams) was dissolved in concentrated sulphuric acid (40 c.c.), and treated with the nitrating mixture (26 c.c.) exactly as in the preceding experiment. The product obtained crystallised from glacial acetic acid in yellow prisms, melting and decomposing at 213—216°:

0·1658 gave 0·2607 CO_2 and 0·0351 H_2O. C = 42·88; H = 2·35.
0·1542 „ 19·1 c.c. N_2 at 22° and 749 mm. N = 13·82.
$C_{11}H_7O_8N_3$ requires C = 42·72; H = 2·27; N = 13·59 per cent.

8-*Nitro*-4 : 6 : 7-*trimethylcoumarin*.—A solution of 4 : 6 : 7-trimethylcoumarin (11 grams) in concentrated sulphuric acid (110 c.c.) was slowly treated at 0° with the nitration mixture (20 c.c.), and then kept at the ordinary temperature for thirty minutes, after which the liquid was poured on ice. A white product was precipitated, which crystallised from glacial acetic acid in colourless needles, melting at 186—187°:

0·2204 gave 0·4958 CO_2 and 0·0946 H_2O. C = 61·36; H = 4·77.
0·2784 „ 14·8 c.c. N_2 at 22° and 761 mm. N = 6·04.
$C_{12}H_{11}O_4N$ requires C = 61·80; H = 4·72; N = 6·01 per cent.

3 : 5 : 8-*Trinitro*-4 : 6 : 7-*trimethylcoumarin*. — A solution of 4 : 6 : 7-trimethylcoumarin (2 grams) in concentrated sulphuric acid (10 c.c.) was treated with the nitrating mixture (10 c.c.) as in the preceding experiment. A crystalline mass formed in the acid solution. After precipitation by pouring into ice-water and crystallisation from glacial acetic acid, the product formed beauti-

fully brilliant, faintly yellow plates, melting and decomposing at about 226°. Darkening took place considerably below this temperature:

0·1285 gave 0·2116 CO_2 and 0·0364 H_2O. C = 44·89; H = 3·15.
0·1723 „ 20·0 c.c. N_2 at 22° and 766 mm. N = 13·25.
$C_{12}H_9O_8N_3$ requires C = 44·58; H = 2·79; N = 13·00 per cent.

The Nitro-derivatives of 4 : 6 : 8-*Trimethylcoumarin.*

5-*Nitro*-4 : 6 : 8-*trimethylcoumarin.*—4 : 6 : 8-Trimethylcoumarin (7 grams) was dissolved in concentrated sulphuric acid (35 c.c.), and treated with the nitrating mixture (15·2 c.c.) at 0°, after which the liquid was kept at the ordinary temperature for thirty minutes and then poured on ice. The product separated from its solution in glacial acetic acid in white needles, melting at 140—141°, and having a peculiar odour:

0·1808 gave 0·4127 CO_2 and 0·0802 H_2O. C = 62·24; H = 4·95.
0·1727 „ 9·5 c.c. N_2 at 22° and 766 mm. N = 6·28.
$C_{12}H_{11}O_4N$ requires C = 61·80; H = 4·72; N = 6·01 per cent.

5 : 7-*Dinitro*-4 : 6 : 8-*trimethylcoumarin.*—4 : 6 : 8-Trimethylcoumarin (5 grams) was dissolved in concentrated sulphuric acid, and treated at 0° with the nitrating mixture (16 c.c.). The liquid was kept for three hours, and then poured into ice-water, when a product was obtained which, after crystallisation from 50 per cent. acetic acid, formed almost white needles, melting at 194°:

0·1659 gave 0·3158 CO_2 and 0·0607 H_2O. C = 51·92; H = 4·06.
0·1408 „ 12·6 c.c. N_2 at 24° and 768 mm. N = 10·15.
$C_{12}H_{10}O_6N_2$ requires C = 51·79; H = 3·60; N = 10·07 per cent.

3 : 5 : 7-*Trinitro*-4 : 6 : 8-*trimethylcoumarin.*—A solution of 4 : 6 : 8-trimethylcoumarin (4 grams) in concentrated sulphuric acid (20 c.c.) was treated at 0° with the nitrating mixture (20 c.c.), as in the preceding experiment. The product crystallised from glacial acetic acid in pale yellow needles, melting and decomposing at about 190°:

0·2272 gave 0·3749 CO_2 and 0·0500 H_2O. C = 45·00; H = 2·44.
0·1632 „ 18·9 c.c. N_2 at 22° and 766 mm. N = 13·23.
$C_{12}H_9O_8N_3$ requires C = 44·58; H = 2·79; N = 13·00 per cent.

7-*Nitro*-5 : 6 : 8-*Trimethylcoumarin.*—5 : 6 : 8-Trimethylcoumarin (1·5 grams) was dissolved in concentrated sulphuric acid (8 c.c.), and treated at 5° with the nitrating mixture (3·6 c.c.). After one hour the liquid was poured on ice, when a solid was produced which crystallised from glacial acetic acid in white needles, melting at 221°:

0·1232 gave 0·2790 CO_2 and 0·0479 H_2O. C = 61·77; H = 4·32.

0·2071 gave 11·5 c.c. N_2 at 24° and 773 mm. N = 6·33.
$C_{12}H_{11}O_4N$ requires C = 61·80; H = 4·72; N = 6·01 per cent.

The Nitro-derivatives of 7-Hydroxycoumarin (Umbelliferone).

8-*Nitroumbelliferone.*—A solution of umbelliferone (2·2 grams) in concentrated sulphuric acid (10 c.c.) was slowly treated at 0° with the nitrating mixture (4 c.c.). After one hour the liquid was poured into ice-water, when a solid was precipitated. This product was extracted twice with small quantities of boiling water, and the residue crystallised from glacial acetic acid. Golden-yellow needles, melting and decomposing at about 245°, were obtained:

0·1151 gave 0·2221 CO_2 and 0·0256 H_2O. C = 52·63; H = 2·47.
0·1231 ,, 7·8 c.c. N_2 at 24° and 747 mm. N = 6·98.
$C_9H_5O_5N$ requires C = 52·17; H = 2·41; N = 6·76 per cent.

6 : 8-*Dinitroumbelliferone.*—Umbelliferone (2 grams) was dissolved in concentrated sulphuric acid (10 c.c.), treated at 0° with the nitrating mixture (9 c.c.), and then warmed gently for five minutes. The cooled liquid was poured on ice, when a solid was obtained which, when crystallised from alcohol, formed yellow needles, sometimes occurring in peculiar serrated tufts, melting at 195—196°:

0·1663 gave 0·2630 CO_2 and 0·0283 H_2O. C = 43·13; H = 1·89.
0·1250 ,, 12·3 c.c. N_2 at 20° and 758 m.m N = 11·23.
$C_9H_4O_7N_2$ requires C = 42·86; H = 1·59; N = 11·11 per cent.

II.—*The Operations involved by the Orientation of the Nitro-derivatives of Coumarin and its Homologues.*

The Oxidation of 3 : 6-*Dinitrocoumarin.*—3 : 6-Dinitrocoumarin (1 gram) was dissolved in dilute aqueous sodium hydroxide with the aid of heat, and the resulting orange-red solution treated at 0° with an alkaline solution of potassium permanganate (2·5 grams). After thirty minutes, sulphurous acid was added until the liquid became clear. The excess of sulphur dioxide was removed by boiling, and the liquid then rendered alkaline with potassium hydroxide. After filtration from the precipitated manganese hydroxide, the liquid was evaporated to a small bulk, acidified with sulphuric acid, and extracted with ether. The ethereal extract, on evaporation, yielded a solid which, when crystallised from water, melted at 228°, and did not depress the melting point of 5-nitrosalicylic acid, prepared by nitrating salicylic acid.

Preparation of 5-*Nitro*-4-*methylsalicylic Acid from* 6-*Nitro*-2-*hydroxy*-p-*xylene.*

A solution of 6-nitro-2-hydroxy-*p*-xylene (1 gram) in dilute potassium hydroxide was treated at 0° with an alkaline solution of potassium permanganate (4·5 grams), and the solution then heated to boiling. Sulphurous acid was added to the liquid until a clear solution was produced, and the manganese salt then precipitated with a slight excess of potassium hydroxide. After evaporating the liquid to a small bulk, sulphuric acid was added in slight excess, when a small quantity of solid separated, which, after crystallisation from water, formed white needles, melting at 212—213°. The yield was very poor:

0·1290 gave 0·2328 CO_2 and 0·0452 H_2O. C=49·22; H=3·89.
0·2182 ,, 13·4 c.c. N_2 at 21° and 762 mm. N=7·01.
$C_8H_7O_5N$ requires C=48·73; H=3·55; N=7·11 per cent.

Preparation of 5-*Nitro*-4-*methylsalicylic Acid from* 6-*Nitro*-7-*methylcoumarin,* 3 : 6-*Dinitro*-7-*methylcoumarin,* 6-*Nitro*-4 : 7-*dimethylcoumarin, and* 3 : 6-*Dinitro*-4 : 7-*dimethylcoumarin.*

The oxidation of each of the above compounds was carried out in the same manner. One gram of the substance was dissolved in dilute potassium hydroxide, the liquid being boiled when necessary. The resulting solution was treated at 0° with the calculated quantity of potassium permanganate in alkaline solution, and the liquid heated to boiling, sulphurous acid being then added until a clear solution was obtained, after which the manganese salt was precipitated with a slight excess of potassium hydroxide. The filtered solution was then evaporated to a small bulk, and acidified with sulphuric acid, when fine white needles were obtained, which, after crystallisation from water, melted at 212—213°. The product was in each case shown to be identical with the 5-nitro-4-methylsalicylic acid prepared in the preceding experiment, by the method of mixed melting points. The yield was best when the nitro-derivatives of 7-methylcoumarin were employed.

Preparation of 3 : 6-*Dinitro*-4 : 5-*dimethylsalicylic Acid from* 5 : 8-*Dinitro*-6 : 7-*dimethylcoumarin.*

A solution of 5 : 8-dinitro-6 : 7-dimethylcoumarin (1 gram) in dilute potassium hydroxide was treated at 0° with an alkaline solution of potassium hydroxide (2·5 grams). Sulphurous acid was then added until the liquid became clear, when from the cooled liquid a plentiful supply of white needles was obtained, which, when crystallised from water, melted and decomposed at about 245°:

0·1166 gave 0·1744 CO_2 and 0·0360 H_2O. C = 40·79; H = 3·58.
0·0941 „ 8·7 c.c. N_2 at 20° and 767 mm. N = 10·67.
$C_9H_8O_7N_2,\frac{1}{2}H_2O$ requires C = 40·75; H = 3·40; N = 10·57 per cent.

Preparation of 5-*Hydroxy*-4 : 6 : 8-*trimethylcoumarin from* 5-*Nitro*-4 : 6 : 8-*trimethylcoumarin.*

5-*Amino*-4 : 6 : 8-*trimethylcoumarin.*—5-Nitro-4 : 6 : 8-trimethylcoumarin (5 grams) was mixed with dilute acetic acid (100 c.c.), and treated gradually with iron filings (5 grams). After boiling for one hour, the liquid was cooled, and the solid which separated was collected. Repeated extraction of the residue with alcohol yielded an abundant crop of yellow needles, melting at 212°:

0·1048 gave 0·2726 CO_2 and 0·0594 H_2O. C = 70·93; H = 6·30.
0·1794 „ 10·4 c.c. N_2 at 19° and 750 mm. N = 6·58.
$C_{12}H_{13}O_2N$ requires C = 70·94; H = 6·40; N = 6·90 per cent.

5-*Hydroxy*-4 : 6 : 8-*trimethylcoumarin.*—5-Amino-4 : 6 : 8-trimethylcoumarin (1·3 grams) was warmed with concentrated hydrochloric acid (6 c.c.), a white hydrochloride being formed, which, on the addition of water (50 c.c.), underwent hydrolysis, and yielded the yellow amine in a finely divided condition. A solution of sodium nitrite (0·5 gram) was added to the cooled liquid, which was then slowly heated. The liquid gradually became clear, and then effervesced and deposited a white product. After boiling for ten minutes, the solid was collected and crystallised from alcohol, when it formed small, white, ill-defined crystals, melting at 246°:

0·1027 gave 0·2654 CO_2 and 0·0570 H_2O. C = 70·46; H = 6·16.
$C_{12}H_{12}O_3$ requires C = 70·59; H = 5·88 per cent.

Preparation of 5-*Hydroxy*-4 : 6 : 8-*trimethylcoumarin from* 2 : 4-*Dimethylresorcinol.*

2 : 4-Dimethylresorcinol (0·6 gram) was mixed with ethyl acetoacetate (0·5 gram), and concentrated sulphuric acid (2 c.c.) then added, the temperature being below 20°. After twenty hours the liquid was poured into ice-water, when a white solid was obtained, which, after crystallisation from alcohol, melted at 246°, and was shown, by the method of mixed melting points, to be identical with the product obtained in the preceding experiment.

Synthesis of 8-*Nitro*-6 : 7-*dimethylcoumarin and* 8-*Nitro*-5 : 6-*dimethylcoumarin.*

4 : 5-*Dimethylsalicylaldehyde* and 5 : 6-*Dimethylsalicylaldehyde.*—*o*-4-Xylenol (20 grams) was dissolved in a solution of sodium hydroxide (44 grams) in water (130 c.c.), and the resulting liquid heated to 60° under reflux. Chloroform (35 grams) was added in small quantities, and the solution heated to boiling for three hours, after which the liquid was acidified with sulphuric acid and distilled in a current of steam. The distillate, which contained a heavy oil, was extracted twice with ether, and the ethereal solution shaken for some time with aqueous sodium hydrogen sulphite, when white, flaky crystals were produced, which were collected, washed with ether, and decomposed by warming with dilute sulphuric acid. The acid solution was extracted with ether, and the extract evaporated to dryness, a white, crystalline mass being thus obtained. This product was dissolved in petroleum (b. p. 40—60°), and the solution left to crystallise, when two kinds of crystals were apparent, namely, yellow, spiky needles, and pink, flaky clusters. The crystals were separated mechanically, and separately crystallised several times from light petroleum, when white, pearly plates of 4 : 5-dimethylsalicylaldehyde, melting at 71°, and almost white, spiky needles of 5 : 6-dimethylsalicylaldehyde, melting at 72°, were obtained.

4 : 5-*Dimethylsalicylaldehyde.*

0·1111 gave 0·2927 CO_2 and 0·0705 H_2O. C = 71·84 ; H = 7·03.

5 : 6-*Dimethylsalicylaldehyde.*

0·1030 gave 0·2711 CO_2 and 0·0641 H_2O. C = 71·78 ; H = 6·91.

$C_9H_{10}O_2$ requires C = 72·00 ; H = 6·67 per cent.

Oxidation of 4 : 5-*Dimethylsalicylaldehyde.*—About equal parts of sodium hydroxide and potassium hydroxide were heated together with a little water in a nickel crucible to 180°, and 4 : 5-dimethylsalicylaldehyde was shaken in little at a time, hydrogen escaping after each addition. The fusion was cooled, dissolved in water, the solution filtered, acidified with dilute sulphuric acid, and finally extracted with ether. On evaporation, the extract yielded a white solid, which, after crystallisation from very dilute alcohol, formed warty masses, which softened at 180°, and melted at 195—199°. This product was shown to be identical with 4 : 5-dimethylsalicylic acid obtained by oxidising ψ-cumenol by the method of mixed melting points.

Oxidation of 5 : 6-*Dimethylsalicylaldehyde.*—This operation, carried out as in the preceding experiment, yielded 5:6-*dimethylsalicylic acid*, which crystallised from dilute alcohol in white needles, melting at 142—143°:

0·1068 gave 0·2536 CO_2 and 0·0568 H_2O. C = 64·75; H = 5·92.
$C_9H_{10}O_3$ requires C = 65·06; H = 6·02 per cent.

3-*Nitro*-4:5-*dimethylsalicylaldehyde*.—A solution of 4:5-dimethylsalicylaldehyde (1 gram) in glacial acetic acid (10 c.c.) was treated with nitric acid (0·5 c.c.) (D 1·4) below 20°. After one hour the solution was poured into ice-water, when a solid was obtained which crystallised from alcohol in white needles, melting at 146—147°:

0·1674 gave 11·0 c.c. N_2 at 23° and 764 mm. N = 7·45.
$C_9H_9O_4N$ requires N = 7·18 per cent.

3-*Nitro*-5:6-*dimethylsalicylaldehyde* was obtained by nitrating 5:6-dimethylsalicylaldehyde in the manner described in the preceding experiment. The product was readily soluble in alcohol, and crystallised from this solvent in deep yellow needles, melting at 86—87°:

0·1387 gave 9·0 c.c. N_2 at 21° and 763 mm. N = 7·42.
$C_9H_9O_4N$ requires N = 7·18 per cent.

8-*Nitro*-6:7-*dimethylcoumarin*. — 3-Nitro-4:5-dimethylsalicylaldehyde (1 gram), anhydrous sodium acetate (1 gram), and acetic anhydride (1·5 grams) were heated together for three hours to 160—170°. The cooled product was extracted from 50 per cent. acetic acid, from which solvent almost white needles, melting at 190—194°, were obtained:

0·0914 gave 5·1 c.c. N_2 at 15° and 760 mm. N = 6·53.
$C_{11}H_9O_4N$ requires N = 6·39 per cent.

8-*Nitro*-5:6-*dimethylcoumarin* was prepared from 3-nitro-5:6-dimethylsalicylaldehyde in the manner described in the preceding experiment. Almost white needles, melting at 191—192°, were obtained:

0·1245 gave 7·1 c.c. N_2 at 20° and 767 mm. N = 6·58.
$C_{11}H_9O_4N$ requires N = 6·39 per cent.

Synthesis of 8-Nitro-7-methylcoumarin.

3-*Nitro*-7-*methylsalicylaldehyde*. — 4-Methylsalicylaldehyde (2 grams) was dissolved in glacial acetic acid (20 c.c.), and treated with nitric acid (0·7 c.c.) (D 1·5) below 20°. After twenty minutes the liquid was slowly heated to 45°, and then poured into ice-water. The precipitated solid, when crystallised from alcohol, formed yellow needles, melting at 126—127°:

0·1176 gave 8·4 c.c. N_2 at 22° and 766 mm. N = 8·16.

$C_8H_7O_4N$ requires N = 7·73 per cent.

8-*Nitro-7-methylcoumarin* was prepared from 3-nitro-4-methylsalicylaldehyde in exactly the same manner as 8-nitro-6 : 7-dimethylcoumarin was obtained from 3-nitro-4 : 5-dimethylsalicylaldehyde (see above). The product separated from its solution in acetic acid in white needles, melting at 165—166°:

0·1080 gave 6·8 c.c. N_2 at 25° and 768 mm. N = 7·10.

$C_{10}H_7O_4N$ requires N = 6·83 per cent.

III.—*The Products of the Action of Alkalis on the Nitro-substituted Coumarins.*

Preparation of 5-*Nitrosalicylaldehyde from* 3 : 6-*Dinitrocoumarin.*—3 : 6-Dinitrocoumarin (5 grams) was dissolved in concentrated ammonia (100 c.c.), and the liquid boiled to expel excess of ammonia. The orange-red solution was cooled to 0°, and slowly treated with dilute hydrochloric acid until precipitation was complete. The solid product, after crystallisation from alcohol, melted at 126°, and was shown by the method of mixed melting points to be identical with the 5-nitrosalicylaldehyde obtained by nitrating salicylaldehyde.

The *sodium* salt was obtained by dissolving 3 : 6-dinitrocoumarin in the least possible quantity of aqueous 15 per cent. sodium hydroxide, and then cooling the solution. Yellow needles were obtained:

0·2987 gave 0·1110 Na_2SO_4. Na = 12·03.

$C_7H_4O_4NNa$ requires Na = 12·17 per cent.

Preparation of 5-*Nitro*-4-*methylsalicylaldehyde from* 3 : 6-*Dinitro*-7-*methylcoumarin.*—3 : 6-Dinitro-7-methylcoumarin was dissolved in concentrated ammonia with the aid of heat, and the resulting orange-red solution acidified with hydrochloric acid, as in the preceding experiment. The product separated from its alcoholic solution in yellow needles, melting at 144—145°:

0·1051 gave 0·2030 CO_2 and 0·0400 H_2O. C = 52·67; H = 4·22.

0·1032 „ 7·4 c.c. N_2 at 22° and 749 mm. N = 8·00.

$C_8H_7O_4N$ requires C = 53·04; H = 3·87; N = 7·73 per cent.

The *oxime*, prepared in the usual way, crystallised from alcohol in yellow needles, melting, sometimes with decomposition, at 207—208°:

0·1223 gave 15·2 c.c. N_2 at 19° and 760 mm. N = 14·29.

$C_8H_8O_4N_2$ requires N = 14·29 per cent.

The *phenylhydrazone* crystallised from dilute acetic acid in yellowish-brown needles, melting at 201—202°:

0·1024 gave 13·5 c.c. N_2 at 15° and 760 mm. N = 15·43.

$C_{14}H_{13}O_3N_3$ requires N = 15·50 per cent.

Preparation of 3 : 6-*Dinitro*-4 : 5-*dimethylsalicylaldehyde from* 3 : 5 : 8-*Trinitro*-6 : 7-*dimethylcoumarin.* — 3 : 5 : 8-Trinitro-6 : 7-dimethylcoumarin (2 grams) was heated with concentrated ammonia (80 c.c.) until solution took place. The cooled orange liquid was carefully acidified with dilute hydrochloric acid, when a solid was obtained which, after crystallisation from alcohol, formed yellow needles, melting at 147—148°:

0·1217 gave 0·2022 CO_2 and 0·0390 H_2O. C = 45·31; H = 3·56.
0·1069 ,, 11·4 c.c. N_2 at 20° and 742 mm. N = 11·90.

$C_9H_8O_6N_2$ requires C = 45·00; H = 3·33; N = 11·67 per cent.

Preparation of ω-5-*Dinitro*-2-*hydroxy*-α-4-*dimethylstyrene from* 3 : 6-*Dinitro*-4 : 7-*dimethylcoumarin.*—Finely powdered 3 : 6-dinitro-4 : 7-dimethylcoumarin (1 gram) and a 15 per cent. solution of sodium hydroxide (30 c.c.) were boiled together for two minutes, and then filtered from a small quantity of undissolved solid. The filtrate was carefully acidified below 0° with dilute hydrochloric acid, when a solid was obtained which was dried at the ordinary temperature and then extracted with benzene. The extract deposited a yellowish-brown, crystalline powder, which melted at 120—121°, and was decomposed by heating with alcohol or water:

0·1452 gave 0·2690 CO_2 and 0·0554 H_2O. C = 50·52; H = 4·24.
0·1475 ,, 15·3 c.c. N_2 at 18° and 752 mm. N = 11·86.

$C_{10}H_{10}O_5N_2$ requires C = 50·42; H = 4·20; N = 11·76 per cent.

The *sodium* salt was prepared by dissolving 3 : 6-dinitro-4 : 7-dimethylcoumarin in the smallest possible quantity of 15 per cent. aqueous sodium hydroxide, the liquid being boiled for not longer than two minutes. The hot solution was filtered through glass wool and cooled to 0°, when a small quantity of yellow needles was deposited, which were washed on a filter with absolute alcohol. The salt is very soluble in water, and deflagrates violently when heated:

0·3129 gave 0·1543 Na_2SO_4. Na = 15·95.

$C_{10}H_8O_5N_2Na_2$ requires Na = 16·31 per cent.

Preparation of 6 : 8-*Dinitrocoumarinic Acid from* 6 : 8-*Dinitrocoumarin.*—6 : 8-Dinitrocoumarin was dissolved in 15 per cent. sodium hydroxide with the aid of heat. The clear red liquid was cooled to 0°, and carefully acidified with dilute hydrochloric acid. The yellow precipitate was collected and dried at the ordinary temperature, when it melted at about 153° with a copious evolution of vapour. Yellow needles were obtained from a solution in ether, but the substance is rapidly converted into 6:8-dinitrocoumarin when its solution in water or alcohol is heated:

0·1562 gave 0·2410 CO_2 and 0·0372 H_2O. C = 42·08; H = 2·64.
0·1003 „ 10·0 c.c. N_2 at 19° and 760 mm. N = 11·46.
$C_9H_6O_7N_2$ requires C = 42·52; H = 2·36; N = 11·02 per cent.

Preparation of 8-Nitro-7-hydroxycoumarinic Acid from 8-Nitro-7-hydroxycoumarin.—8-Nitro-7-hydroxycoumarin was dissolved in aqueous 15 per cent. sodium hydroxide, the temperature being raised to 30° for one minute. The red liquid was acidified at 0° with dilute hydrochloric acid, when it deposited a fine scarlet powder, which was dried at the ordinary temperature, and crystallised from dry ether. The scarlet needles which separated gradually became yellow when heated, and finally melted and decomposed at 240—245°. The yellow product was shown to be 8-nitro-7-hydroxycoumarin by the method of mixed melting points. The scarlet compound was also found to be completely converted into the yellow parent coumarin when heated for some time to 150°:

0·1464 gave 0·2562 CO_2 and 0·0456 H_2O. C = 47·73; H = 3·46.
0·1624 „ 8·9 c.c. N_2 at 23° and 763 mm. N = 6·20.
$C_9H_7O_6N$ requires C = 48·00; H = 3·11; N = 6·22 per cent.

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CXXIX.—*Estimation of Sodium and Caesium as Bismuthinitrites. Part I. Estimation of Sodium.*

By Walter Craven Ball.

In a recent paper (Trans., 1909, **95**, 2126) the author showed that sodium salts produce a precipitate of sodium cæsium bismuthinitrite, $9CsNO_2,6NaNO_2,5Bi(NO_2)_3$, when added to a solution of potassium nitrite containing bismuth nitrate and cæsium nitrate. No corresponding potassium salt appears to exist, and the sodium salt, precipitated from solutions containing several thousand times as much potassium as sodium, is free from the former metal.

The above-mentioned paper, which dealt primarily with the detection of sodium, included also the results of a few estimations of sodium as sodium cæsium bismuthinitrite, which indicated that the method might prove to be an accurate one. As will be seen from the appended tables of results (tables A and B, pp. 1413, 1414), this is the case, provided that the reagent is made up as described, and that the precautions mentioned with regard to collecting and washing the precipitate are observed.

A great advantage of the method is that none of the metals commonly associated with sodium in analysis, such as calcium, magnesium, lithium, and ammonium, interfere, at least when present in the amounts used in these experiments, and, as mentioned above, traces of sodium may be estimated in potassium salts. Another advantage is that the precipitate contains only 3·675 per cent. of sodium, so that 1 milligram of the metal yields 27·2 milligrams of precipitate.

On the other hand, chlorides should not be present in greater concentration than $N/5$, or bismuth oxychloride may separate. Phosphates, if present in more than traces, must be removed.*

Iodides interfere, as also do citrates and the salts of some other hydroxy-acids. Sulphates, nitrates, nitrites, acetates, and formates do not interfere. Most of the heavy metals, particularly silver, must be absent. The method is particularly applicable to the estimation of small amounts of sodium in mixtures such as sea-water; for example, the sodium in 0·2 c.c. of sea-water was determined directly with fair accuracy. It may therefore be found useful in the analysis of soils, etc., and in physiological chemistry.

The estimation is not a costly one, and the cæsium, the only expensive ingredient, may be easily obtained pure from the residues by the addition of silver nitrate, which precipitates a very insoluble salt, silver cæsium bismuthinitrite.† This, on heating and subsequent extraction with water, yields a pure cæsium salt.

Preparation of the Reagent.—This is made by adding bismuth nitrate and cæsium nitrate to a solution of *pure* potassium nitrite. As all the samples of this salt were very impure, generally containing much sodium, and as it cannot be purified to any extent by recrystallisation, the author prepared it by passing nitrous fumes into a concentrated solution of potassium carbonate, which salt can be bought almost free from sodium.

Thirty grams of the pure nitrite ‡ are dissolved in a little water, and to this are added 3 grams of bismuth nitrate dissolved in a little dilute nitric acid (the solution used contained 40 grams of the crystallised salt made up to 50 c.c. with approximately 2*N*-nitric acid; 3·75 c.c. of this contained 3 grams of the nitrate). Should the resulting yellow liquid be turbid, which may occur if the nitrite contains free alkali, dilute nitric acid must be added until it is clear. Then 16 c.c. of a 10 per cent. solution of cæsium nitrate are added, and the volume made up to 100 c.c. with water, or, if turbid, with water and a little nitric acid.

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* This may be done by warming to 100° with a solution of potassium nitrite (pure) to which bismuth nitrate has been added.

† If excess of silver nitrate be added, this will contain also silver potassium bismuthinitrite, which may be removed by reprecipitation.

‡ This can now be obtained, almost free from sodium, from Messrs. Morson.

Even when made from the purest reagents obtainable, this liquid will slowly deposit a small, yellow precipitate of sodium cæsium bismuthinitrite. The liquid should be kept for two days, and then filtered from the precipitate, when it is then practically free from sodium. If exposed to the air, a white scum appears on the surface of the reagent, probably owing to two different reactions:

$$(1)\ \mathrm{Bi(NO_2)_3 = BiONO_3 + 2NO.}$$

$$(2)\ \mathrm{2Bi(NO_2)_3 + O_2 + 2H_2O = 2BiONO_3 + 4HNO_2.}$$

It may be kept for some weeks in a stopped cylinder provided with a Bunsen valve, especially if protected from the air by coal gas or a layer of paraffin.

The proportion of potassium nitrite may be lowered to 25 or 20 grams per 100 c.c., but such a reagent does not keep so well, and appears to be less trustworthy. The amount of bismuth nitrate may be increased to 6 grams or more, but again this reagent is much less stable, although it causes a more rapid precipitation; less than 3 grams of bismuth nitrate per 100 c.c. must not be used. Addition of cæsium nitrate beyond 1·6 to 1·8 grams per 100 c.c. of reagent causes the weight of precipitate to be too large. More than 2 grams of cæsium nitrate per 100 c.c. produces a precipitate of hexagonal plates of cæsium bismuthinitrite, and it is possible that an admixture of this compound is the cause of the too high weight of precipitate obtained when the reagent contains more than 1·6 to 1·8 grams of cæsium nitrate per 100 c.c.* It is found also that the precipitate of cæsium bismuthinitrite is formed with lower concentrations of cæsium when the concentration of potassium nitrite is also lowered; thus a reagent containing 30 grams of potassium nitrite and 2 grams of cæsium nitrate per 100 c.c. deposited no hexagonal plates, whereas one containing 15 grams of potassium nitrite and 2 grams of cæsium nitrate gave more than 1 gram of cæsium bismuthinitrite.

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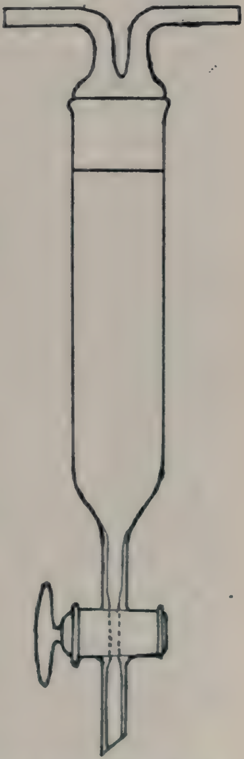
* These precipitates, however, when examined with the microscope, appear to be free from the hexagonal crystals of cæsium bismuthinitrite and to be homogeneous. Another possible explanation is that various sodium cæsium bismuthinitrites exist in which the atomic ratio of cæsium to sodium varies from 3 : 2, as in the formula $\mathrm{9CsNO_2,6NaNO_2,5Bi(NO_2)_3}$, to 2 : 1, as in the formula $\mathrm{2CsNO_2,NaNO_2,Bi(NO_2)_3}$. The ratio of cæsium to sodium was determined in some of these precipitates, and approached, but never quite reached, the higher value. The point is a difficult one to decide.

The reagents should therefore be made up as described. If a reagent giving a more rapid precipitation is required, the author's experiments indicate that this might perhaps be effected by using a greater concentration of cæsium, and finding experimentally a factor for converting the weight of precipitate into weight of sodium.

Of the three metals, sodium, cæsium, and bismuth, any one may probably be completely precipitated by the presence of a large excess of the other two.

One c.c. of the above reagent will precipitate 0·5 to 0·7 milligram of sodium. The reagent thus prepared may be used for the detection of sodium, instead of that described in the former paper, as it is more stable, and almost equally delicate.



Method of Precipitation.

The reagent must be kept as much as possible from contact with the air, and therefore the precipitation must be conducted in a vessel filled with coal gas or other inert gas. The author uses a cylindrical tapped funnel, as illustrated, provided with a stopper containing two tubes for the replacement of air by coal gas. This stopper may be of rubber, but glass is better, as the rubber is attacked by the nitrous fumes. These cylinders may be roughly graduated so that various quantities of the reagent may be measured into them. Fairly accurate results may also be obtained by dispensing with this apparatus and using a conical beaker, finally washing out the precipitate with the mother liquor; but unless this is very carefully done, the results are not so accurate.

Suppose that a quantity of 10 milligrams of sodium is to be estimated. In this case 20 to 25 c.c. of the reagent are placed in a cylinder (capacity about 50 c.c.), 1 c.c. of dilute nitric acid (about $2N$) added, and the sodium salt, dissolved in 5 c.c. or less of water, is added. The mixture is well stirred (a glass rod expanded at the end answers best), coal gas passed into the cylinder for a few seconds, and the tubes closed, one by a rubber cap, the other by a Bunsen valve.

The sodium cæsium bismuthinitrite will begin to separate within a minute or two, and will collect in the lower part of the cylinder. After twenty-four to forty-eight hours (twenty-four hours' standing gives results which are generally a little low, but it will be seen from the appended figures that the difference is very small), the precipitate is stirred with a stout wire, so that it will easily pass through the tap. This is then opened, and the precipitate and liquid allowed to run into a small Gooch crucible, with a fairly thick asbestos felt. The liquid should be run into the Gooch crucible at such a rate that the precipitate is covered with the liquid during the filtration. The filtrate is received in a clean filter flask, poured back as quickly as possible into the cylinder, any precipitate remaining on the walls of the cylinder stirred into the liquid with a rubber-tipped glass rod, and the filtration repeated.

The essential point is the complete transference of the precipitate from the cylinder to the crucible, with the least possible exposure to the air, and this requires some care to accomplish. The production of a small amount of scum on the sides of the cylinder during the second filtration has no perceptible effect on the estimation. Unless the first filtrate is not clear, it is not necessary again to filter the whole of it, but a little will be required to wash out any precipitate adhering to the sides of the cylinder.

The precipitate is then washed rapidly by suction with 5 c.c. of a mixture of equal volumes of acetone and water (10 c.c. if the precipitate be a large one) contained in a small wash bottle, and then with pure acetone. The washing liquid must be directed against the sides of the crucible, in order to wash down any adhering traces of the reagent. Finally, the suction is stopped, some acetone is put into the crucible, and suction again started slowly. The precipitate is then dried at 100° (fifteen minutes suffices), and weighed.

An alternative method is to use 5 to 10 c.c. of a 5 per cent. solution of pure potassium nitrite (containing no free alkali), and then acetone as above.

Experiments were made with many other washing agents; none completely removed the mother-liquor without at the same time dissolving a little of the precipitate. The two mentioned yield the best results; a first washing with 60 to 70 per cent. acetone or with 5 per cent. sodium nitrite was generally less satisfactory. Acetone itself has no action on the precipitate.

For each 5 c.c. of 50 per cent. acetone used, 0·07 milligram may be added to the amount of sodium found, and for each 5 c.c. of 5 per cent. potassium nitrite about 0·1 milligram, to correct for the amount of precipitate dissolved. The results of some deter-

TABLE A.—*Results of Sodium Estimations, using 50 per cent. Acetone or 5 per cent. Potassium Nitrite, and subsequently Pure Acetone, to wash the Precipitate.*

No. of experiment.	Sodium salt used.	C.c. of salt solution.	C.c. of reagent used.	Time allowed for precipitation, hours.	Sodium taken, gram.	Sodium found, gram.	Sodium found, corrected for loss in washing, gram.	Method of washing, and remarks.
1	Nitrate	5	40	24	0·0247	0·0249	0·0250	50 per cent. acetone, then acetone
2	,,	2	20	21	0·0099	0·0096	0·0097	,, ,, ,,
3	,,	2	20	24	0·0079	0·0077	0·0077	,, ,, ,,
4	,,	2	20	24	0·0079	0·0079	0·0080	,, ,, ,,
5	,,	2	20	48	0·0079	0·0083	—	This result, decidedly too high, may be due to incomplete washing 50 per cent. acetone, then acetone
6	,,	4	25	48	0·0157	0·0152	0·0153	,, ,, ,,
7	,,	7	20	72	0·0099	0·0098	0·0099	,, ,, ,,
8	,,	2	20	94	0·0079	0·0078	0·0079	,, ,, ,,
9	,,	2	20	96	0·0079	0·0078	0·0079	,, ,, ,,
10	Acetate	2	20	24	0·0086	0·0087	0·0088	,, ,, ,,
11	,,	7	60	48	0·0301	0·0307	0·0309	,, ,, ,,
12	,,	10	80	48	0·0430	0·0417	0·0420	,, ,, ,, The quantity of dilute nitric acid added was, in this experiment, larger than usual
13	,,	2	20	70	0·0086	0·0086	0·0086	50 per cent. acetone, then acetone
14	,,	1	10	72	0·0043	0·0040	0·0041	,, ,, ,,
15	,,	2	20	72	0·0086	0·0087	0·0088	,, ,, ,,
16	Chloride	2	20	24	0·0063	0·0061	0·0062	,, ,, ,,
17	,,	2	20	72	0·0054	0·0054	0·0055	5 per cent. potassium nitrite, then acetone
18	Sulphate	5	20	28	0·0130	0·0127	0·0131	10 per cent. potassium nitrite, then acetone

A number of estimations, in which the precipitates were washed with solutions of sodium nitrite of 1 to 5 per cent. strength, are not included, as the results, although they agreed fairly well with the above, were not so concordant. As solutions of sodium nitrite have little action on the precipitate, it was thought that they would suffice to remove all mother-liquor from the precipitate, and that, in the short time required for the filtration, no appreciable error would be caused by further precipitate formed by the sodium nitrite and the small quantity of mother-liquor adhering to the precipitate. The method was, however, given up as unsatisfactory.

minations are given in tables A and B, experiments in which other washing liquids than those recommended were used having been omitted, as they did not give such concordant results.

After a little experience, very concordant values may be obtained. For example, three determinations, similar in all respects, of equal quantities of sodium gave:

(1) Precipitate = 0·2069 gram = 0·00760 gram Na.
(2) ,, = 0·2062 ,, = 0·00758 ,,
(3) ,, = 0·2065 ,, = 0·00759 ,,

Table B.—*Estimations of Sodium in Presence of a Mixture of Potassium Sulphate, Magnesium Nitrate, Ammonium Nitrate, Lithium Nitrate, Calcium Chloride, and Rubidium Chloride.*

No. of experiment.	Sodium salt used.	Substances added, gram.	Time allowed for precipitation, hours.	Sodium taken, gram.	Sodium found, gram.	Sodium found, corrected for loss in washing, gram.
1	Nitrate	0·040 potassium sulphate 0·024 magnesium nitrate 0·008 ammonium ,, 0·004 lithium ,, 0·004 rubidium chloride 0·004 calcium ,,	48	0·0058	0·0060	0·0060
2	,,	As in experiment 1	49	0·0060	0·0057	0·0058
3	,,	As in experiments 1 and 2	72	0·0058	0·0059	0·0059
4	,,	0·020 potassium sulphate 0·012 magnesium nitrate 0·004 ammonium ,, 0·002 lithium ,, 0·002 rubidium chloride 0·002 calcium ,,	72	0·0079	0·0075	0·0076

Sea Water.—Some sea-water was diluted to one-fifth, and the sodium estimated in 2 c.c. Calculated as sodium chloride, the results of three estimations were:

2·6 grams of sodium chloride per 100 grams of sea-water.
2·4 ,, ,, ,, ,, ,, ,,
2·5 ,, ,, ,, ,, ,, ,,

The specific gravity of the sample was 1·028, and the total amount of solids 3·393 grams per 100 grams of sea-water. (Average values for similar sea-water are 2·64 grams sodium chloride per 100 grams; specific gravity, 1·026; total solids, 3·39 grams per 100 grams.)

Part of the cost of this investigation was defrayed by a grant from the Chemical Society, for which the author desires to express his thanks.

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CXXX.—*Carthamine. Part I.*

By Tokuhei Kametaka and Arthur George Perkin.

Safflower, the *Carthamus tinctorius*, at one time a most important red dyestuff, on the advent of safranine quickly fell into disuse throughout Europe, but nevertheless large quantities are still cultivated, more especially in India, and employed for dyeing and pigment manufacture. The red colouring matter, carthamine, is present in the flowers to the extent of 0·3 to 0·6 per cent. (Salvetat, *Ann. Chem. Phys.*, 1849, [iii], **25**, 337), together with a very large amount of a soluble yellow substance, which is useless and even harmful in the dyeing operation. Although carthamine is specially interesting on account of its substantive dyeing properties, it appears to have received but little attention, and this is probably due to the tedious and expensive character of the peculiar operations which are necessary for its isolation from the plant. For this purpose it is usual to extract the flowers, which have been previously washed with water in order to remove the yellow substance, with dilute sodium carbonate solution. If the alkaline extract be now acidified with citric or tartaric acids, the carthamine is precipitated in so finely divided a condition that it cannot be successfully collected, and to obviate this difficulty cotton or flax is dyed with the colouring matter by immersion in the alkaline liquid, followed by a subsequent acidification of the dye-bath. The carthamine is now removed from the dyed cotton by means of sodium carbonate solution, and is deposited from this extract by means of an organic acid in a purer and more granular form. The crude material employed in this investigation was procured from Kyoto in Japan, in which country it finds considerable employment as a cosmetic. For its preparation the safflower, which is imported both from China and India, is subjected to a process very similar to that outlined above, the alkali being supplied by plant-ash extract, and the organic acid from the juice of the Japanese plum. Considerable experience appears to be necessary in neutralising the alkaline extract of the plant, and also of the dyed cotton, for, should this be carried beyond a certain point, a brown impurity is subsequently deposited, which causes a considerable deterioration of the brilliancy of the colouring matter. The yield of dyestuff varies according to the quality of the plant, but according to figures given by the Japanese maker, 80 lbs. of the dried flowers usually yield about 285 grams of the crude carthamine.

Samples described as carthamine were also procured by purchase from the Continent, but these were useless for our purpose, and contained little or none of the colouring matter. Although no doubt originally derived from safflower, the dye had evidently been decomposed during the extraction process; moreover, it would appear that some novel method of isolation had been attempted, for on incineration it yielded 15·7 per cent. of ash, mainly calcium carbonate, whereas the ash of the Japanese product (12·8 per cent.) consisted almost entirely of potassium carbonate.

Preisser, the first to investigate carthamine (*J. pr. Chem.*, 1844, [i], **32**, 142), describes this substance as colourless needles, which, by air-oxidation in the presence of alkali, were converted into carthamein, the true colouring matter. Schlieper (*Annalen*, 1846, **58**, 357), however, considered that Preisser's statements were absolutely incorrect, and he isolated carthamine in the form of green, iridescent, red crusts, or as a granular, greenish-red powder, to which he assigned the formula $C_{14}H_{14}O_7$. When digested with boiling alcohol, it was converted into a yellow compound having the composition $C_{14}H_{14}O_9$. According to Malin (*Annalen*, 1840, **36**, 117), carthamine gives *p*-hydroxybenzoic acid when digested with boiling potassium hydroxide solution.

Much more recently Radcliffe (*J. Soc. Dyers*, 1897, **13**, 158), by extracting an air-dried commercial paste extract of safflower with methyl alcohol, subsequently evaporating the solution, and adding hot water, obtained a product crystallising in red, iridescent needles, melting at 168—169° (provisional), which, when exposed to sunlight, changed to a red powder. A study of the absorption spectra of solutions of this substance, and an account of its general properties, are described in his paper, but he reserved analytical details for a later communication.

Although carthamine has proved to be somewhat more stable than was anticipated, the ease with which it undergoes alteration in the presence of most reagents, together with its expensive nature, has shown that the investigation of this compound is an extremely difficult problem. The communication of the somewhat meagre results given below, and which can only be regarded as of a preliminary nature, is rendered necessary by the fact that our joint work has now to cease.

EXPERIMENTAL.

In order to repeat Radcliffe's experiments (*loc. cit.*), some portion of the Safflower extract was procured from Japan in the condition of a bright red paste, but the main bulk consisted of the dried substance in the form of green, iridescent fragments still attached to the silken material, on which it had evidently been drained.

The paste, after drying at the ordinary temperature, was exhausted in the finely divided condition with methyl alcohol, and after concentration the solution was treated with hot water. On standing, fine, hair-like needles separated out, which, when collected and dried, formed about 6 per cent. of the original material, and evidently corresponded with Radcliffe's preparation.* Examination showed that not only was the undissolved substance, which still contained a large quantity of the colouring matter, most sparingly soluble in hot methyl alcohol, but that the dried crystals were also but little attacked by this solvent, so that a recrystallisation in this manner was difficult to carry out. It accordingly seems probable that in the colloidal condition carthamine is somewhat readily dissolved by boiling alcohol, but otherwise it is not, and bearing in mind Schlieper's statement (*loc. cit.*), that carthamine is decomposed by long boiling with alcohol, this method of purification, which involved a long digestion with very large quantities of the solvent, was abandoned. Radcliffe found that when the safflower extract he employed was evaporated to dryness on the water-bath, the heating destroyed the colouring matter, but as experiments with the Japanese product did not confirm this point, it is evident that in the former case some special impurity of the extract must have been responsible for this change.

In order to devise a more ready method for the purification of the crude material, repeated trials were carried out, and ultimately the use of pyridine was adopted. In this liquid, carthamine somewhat readily dissolves, but owing to the sensibility of the colouring matter, it is preferable to conduct the extraction process and the subsequent operations at as low a temperature as possible. Forty grams of the finely powdered material were treated with 400 c.c. of pyridine (Kahlbaum's I.) on the water-bath for about fifteen minutes, and the undissolved residue treated in a similar manner, first with 200 c.c. of pyridine, and finally with 100 c.c. of the same solvent, or until the filtrate was not longer red coloured. The united pyridine extracts were now concentrated under diminished pressure (40 mm.) at 60—65° to a small volume, and warm water was then added until a faint turbidity occurred. On keeping, a beautiful semi-solid, crystalline mass was obtained, and this was collected and washed with a little water. The product thus obtained had a very pure appearance, and averaged, when dry, 22·5 grams, or a yield of 56 per cent., whereas the insoluble residue was 10·5 grams, or 26 per cent. of the original material.

Examination showed that the crystalline carthamine contained, not only a trace of mineral matter, but some quantity of a colourless wax, and to remove the latter the crystals were extracted in a Soxhlet apparatus, first with chloroform and then with ether. As carthamine gradually suffers alteration in the presence of hot dilute mineral acid, the inorganic matter could not be well removed by such a treatment, but experiment indicated that this could be effected by repeated crystallisation from pyridine, and washing with water. Unfortunately, however, it is difficult to recover satisfactorily the colouring matter from the pyridine mother liquors, and as in each operation but 60 per cent. of the dissolved substance separates on cooling, the loss of the very expensive carthamine is serious, and the yield of the chemically pure compound does not average more than 25 to 30 per cent. of the original dry extract.

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* These crystals contained a large amount of mineral matter, apparently in combination with the carthamine.

When purified in this manner, carthamine contains pyridine of crystallisation, which is not removed by washing the crystals with ether or benzene. For analysis, it was dried at 125° or 160°, and when anhydrous was exceedingly hygroscopic, a fact which rendered the weighing operations somewhat difficult:

Found, $C=58{\cdot}16$, $58{\cdot}47$, $58{\cdot}33$, $57{\cdot}91$; $H=4{\cdot}87$, $4{\cdot}23$, $4{\cdot}83$, $4{\cdot}90$.
$C_{14}H_{14}O_7$ (Schlieper, *loc. cit.*) requires $C=57{\cdot}14$; $H=4{\cdot}76$ per cent.
$C_{15}H_{14}O_7$ requires $C=58{\cdot}82$; $H=4{\cdot}57$ per cent.
$C_{25}H_{24}O_{12}$ „ $C=58{\cdot}14$; $H=4{\cdot}65$ „

As obtained in this way, carthamine consists of bright scarlet-coloured, prismatic needles, which melt and decompose at about 228—230°, a point which is considerably higher than that given provisionally by Radcliffe (*loc. cit.*). According to Schlieper, and also to Radcliffe, carthamine is freely soluble in cold alcohol, and this is curious because the chemically pure substance, although giving with ethyl and methyl alcohols a coloured solution in the cold, was only sparingly soluble in these liquids, even on boiling. On the other hand, it is somewhat more readily dissolved by methylated spirit, but is almost insoluble in acetone, in which again Radcliffe states it is freely soluble. Carthamine dissolves in dilute alkali hydroxides, sodium carbonate, and ammonia with an orange colour, and on addition of acid is reprecipitated unchanged, but the product exhibits the somewhat unfortunate characteristic of this colouring matter that when collected it cannot be washed with water without passing through the paper. If carthamine is, however, dissolved in a little strong ammonia, the solution treated with glacial acetic acid, and then with its own volume of alcohol and boiled, the colouring matter is thus deposited in a beautifully crystalline condition. Cold alkaline solutions of the substance suffer oxidation on exposure to the air, with the formation of a brown liquid, from which acids throw down a black-coloured precipitate.

With sulphuric acid, carthamine forms a dull red-coloured solution, which, after heating to 100°, gives with water a violet precipitate, possessing feeble mordant dyeing properties, and is soluble in alkalis with a green coloration. Although carthamine is not perceptibly attacked by cold dilute acids, on heating an alteration occurs with formation of a dull brown precipitate, which does not appear to be susceptible to crystallisation. Hydrochloric acid (33 per cent.), in the presence of boiling acetic acid, reacts somewhat similarly to sulphuric acid, and the product is soluble in alkalis with a green tint. Alcoholic lead acetate gives with carthamine a bright scarlet precipitate soluble in water, and alcoholic ferric chloride a deep brown coloration. When examined by Zeisel's method, no trace of a methoxy-group could be obtained. As was to be expected from its behaviour with lead acetate, carthamine is devoid of affinity for mordants, but is *per se* a substantive dyestuff toward silk, wool, and cotton.

Action of Nitric Acid.—Nitric acid (D 1·5) dissolves carthamine with a deep orange coloration, from which water throws down a yellow precipitate. The acid liquid, when evaporated to a small bulk, on cooling solidified to a crystalline mass, which was drained on a tile, and recrystallised from water. It consisted of pale yellow leaflets, melting at 118—120°, and had all the properties of picric acid.

Action of Fused Alkali.—Carthamine was heated with ten times its weight of potassium hydroxide and a little water to 210—220° for about fifteen minutes. The pale brown-coloured melt was dissolved in water, the solution neutralised with acid, extracted with ether, and the extract evaporated. A crystalline mass was thus obtained, which possessed a strong odour of acetic acid, and in order to isolate a phenol, if such was present, it was dissolved in a solution of sodium hydrogen carbonate, and the liquid agitated with ether. As this gave a negative result, the solution was again neutralised with acid, the substance recovered by means of ether, and purified by crystallisation from water.

It consisted of colourless needles, melting at 208—210°, and had all the properties of *p*-hydroxybenzoic acid. Malin's statement (*loc. cit.*) is thus confirmed.

Action of Dilute Alkali.—Experiments were now carried out on the action of boiling potassium hydroxide solutions (50 c.c.), varying in strength from 50 per cent. to 1 per cent., on carthamine (1 gram), from which it became evident how very sensitive this colouring matter is under these conditions. The solutions quickly became brownish-yellow coloured, and, on neutralisation with acid, a brown precipitate (A) separated, which varied in quantity according to the concentration of the reagent and the length of the digestion. Thus, by heating with 50 per cent. alkali for half an hour, but a trace of this brown product was obtained, whereas with 5 per cent. alkali the yield was about 50 per cent. It was collected, the clear liquid repeatedly agitated with ether, and the ethereal extract evaporated to a small bulk. The residual solution was treated with its own volume of benzene, and slowly concentrated, with the result that at first a small quantity of a resin separated, which was filtered off, and on further distillation minute crystals were deposited. These were collected and crystallised from water, in which they were very sparingly soluble, until colourless. (Found, $C=65{\cdot}73$; $H=4{\cdot}95$. $C_9H_8O_3$ requires $C=65{\cdot}85$; $H=4{\cdot}88$ per cent.)

It consisted of long needles, which melted at 207—208°, and gave with ferric chloride a brown coloration. These properties suggested that it was *p*-coumaric acid, and this was confirmed by a comparison with the synthetical product, prepared according to Eigel's directions (*Ber.*, 1887, **20**, 2530).

The benzene mother liquors from which the coumaric acid had separated were concentrated to a very small volume, and on keeping overnight became semi-solid, owing to the separation of crystals. These were collected, drained on porous porcelain, and crystallised from water with the aid of animal charcoal. When obtained in this way the substance melted at 113—114°, but as it still contained a yellow impurity it was carefully sublimed between watch glasses, and finally crystallised from water. (Found, $C=68{\cdot}76$; $H=4{\cdot}96$. $C_7H_6O_2$ requires $C=68{\cdot}85$; $H=4{\cdot}92$ per cent.) It now fused at 115—117°, gave with ferric chloride a pale violet coloration, and was identified as *p*-hydroxybenzaldehyde by comparison with the synthetical product.

The brown, resinous compound (A), also produced by the action of the alkali on carthamine, could not be crystallised, and was therefore again submitted to the action of the boiling dilute alkali. In this manner it yielded a further quantity of *p*-coumaric acid and *p*-hydroxybenzaldehyde, and it thus appears likely that no third ether soluble product can be obtained from carthamine by this reaction.

Carthamine is also decomposed when digested with strong boiling barium hydroxide solution, and there is thus produced a trace of *p*-coumaric acid and *p*-hydroxybenzaldehyde, together with a large quantity of brown, resinous substance.

Action of Hydrogen Peroxide.—Two grams of carthamine, dissolved in 200 c.c. of 1 per cent. sodium carbonate solution, were treated with 3·8 c.c. of hydrogen peroxide (Merck's perhydrol), and the liquid kept overnight. The resulting yellow solution was acidified, repeatedly extracted with ether, and the ether evaporated. The yellow, crystalline residue was purified by crystallisation from water, in which it was very sparingly soluble, employing animal charcoal. (Found, $C=65·73$; $H=4·95$. $C_9H_8O_3$ requires $C=65·85$; $H=4·88$ per cent.) It melted at 207—208°, and was found to consist of *p*-coumaric acid. Experiments on the oxidation of carthamine with perhydrol were also carried out in the presence of acetic acid. Addition of water caused the separation of a yellow, gelatinous precipitate, soluble in alkalis with a yellow colour, and which separated from methyl alcohol and water in an amorphous condition. The filtrate contained *p*-coumaric acid.

Benzoylcarthamine.—One gram of carthamine, dissolved in 15 c.c. of pyridine, was treated with 11 c.c. of benzoyl chloride in the usual manner. The next day addition of water caused the separation of a resinous mass, which was purified by adding alcohol to its solution in acetone, and repeating the same operation two or three times. Two distinct preparations were made, but up to the present attempts to crystallise this compound have failed. To be certain that it was completely benzoylated, it was submitted to the action of benzoic anhydride at 170° for a few minutes, and recovered by precipitation from alcohol:

Found, $C=70·85$; $H=4·44$; $C=70·98$; $H=4·42$; $C=70·92$; $H=4·55$.

$C_{25}H_{17}O_{12}(C_7H_5O)_7$ requires $C=71·38$; $H=4·18$ per cent.
$C_{25}H_{18}O_{12}(C_7H_5O)_6$ „ $C=70·52$; $H=4·21$ „

It consisted of a pale red, amorphous powder, which sintered at 210°, and melted and decomposed at about 230—232°.

Attempts to prepare a crystalline acetyl derivative * from carthamine by Deninger's method have as yet been unsuccessful. By the action of boiling acetic anhydride, the acetylation is accompanied by decomposition, the solution rapidly darkens, and gives an indefinite amorphous compound.

On account, also, of the extreme sensitiveness of carthamine to alkali, it does not appear to be possible to methylate this colouring matter, either by means of methyl sulphate or methyl iodide, without at least some portion of the product becoming decomposed, and the result of numerous experiments indicated that this was the case. In the hope of obtaining a more satisfactory result, the action of an ethereal solution of diazomethane on carthamine was studied. The well-dried colouring matter suspended in anhydrous ether was treated with excess of this reagent, causing the evolution of gas and the gradual change of the substance from red to yellow. After keeping overnight, the product was collected, but on examination the greater bulk of the substance was found to be insoluble in all solvents, and in appearance somewhat resembled cork. By Zeisel's method the presence of methoxy-groups could not be detected. A repetition experiment gave the same result, and it was evident that in this case the behaviour of the diazomethane is abnormal. In addition to this product, a small quantity of yellow, amorphous substance was also formed, which was soluble in alcohol, gave on analysis OMe = 28·7 per cent., and possibly contained a true methyl ether, but the yield was not sufficiently good to permit of its further examination.

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* The amorphous substance thus produced gave $C=57·95$, $H=4·32$, and agrees fairly well with $C_{25}H_{17}O_{12}(C_2H_3O)_7$, which requires $C=57·78$; $H=4·68$ per cent. Its purity was, however, doubtful.

A study was now made of the oxidation of the crude methylation product of carthamine, prepared by means of methyl sulphate. Three grams of the dark-coloured powder were shaken with 80 c.c. of 1 per cent. sodium carbonate solution, and 10 c.c. of Merck's perhydrol were then added. After keeping overnight, the yellow liquid was filtered, and the filtrate extracted with ether. On evaporating the ether, an orange-coloured, crystalline mass was obtained, which possessed a strong aromatic odour. The product was crystallised from alcohol, employing animal charcoal, and was obtained in pale yellow needles, melting at 170°. (Found, C = 67·00; H = 5·84. $C_{10}H_{10}O_3$ requires C = 67·41; H = 5·62 per cent.) This acid was found to consist of *p*-methoxycinnamic acid. The alcoholic mother liquor contained the highly aromatic substance above referred to, and this could be isolated on account of its insolubility in sodium hydrogen carbonate solution. The quantity obtained has as yet been too small for analysis, but it most probably consists of *p*-methoxycinnamaldehyde, a substance which has apparently not yet been synthesised.

Oxidation with Chromic Acid.—The oxidation of the crude carthamine methyl ether with chromic acid at the ordinary temperature was also carried out. The main product of the reaction, soluble in ether, was a colourless, crystalline acid, which melted at 180°, and was found to consist of anisic acid. A small quantity of a second substance, which was insoluble in sodium hydrogen carbonate solution, was also isolated, and this possessed the characteristic odour of anisaldehyde.

According to Schlieper (*loc. cit.*), when carthamine is digested with boiling alcohol, it is slowly converted into a yellow substance of the formula $C_{14}H_{14}O_9$, and Radcliffe (*loc. cit.*) also states that it was noted that alcoholic solutions of carthamine rapidly decompose with the production of a yellow colouring matter. Attempts to repeat these experiments were, curiously enough, quite unsuccessful, and no yellow substance was produced from carthamine by digesting its solutions in methyl alcohol, ethyl alcohol, or the ordinary laboratory spirit at the boiling point for long periods, or under pressure at 100° in sealed tubes. It is most likely, therefore, that the production of this yellow substance must have arisen from the action of some impurity present in the carthamines of Schlieper and Radcliffe, or in the alcohol they employed, although experiment showed that as regards the latter this could not have been due to acetone. On the other hand, it has been shown that Radcliffe's substance, both in melting point and solubility, differs markedly also from pure carthamine, and it suggests itself as possible that his compound was a potassium salt of the colouring matter, and that this, as one would anticipate, is less stable than carthamine itself.

That carthamine shows a tendency to give a yellow product was ascertained during some experiments on its acetylation * in the presence of sulphuric acid. Thus, if the colouring matter is suspended in acetic anhydride to which a few drops of sulphuric acid have been added, and the mixture kept for some days or is heated for a short time on the water-bath, an orange-brown substance is precipitated when the product is poured into water. By extracting this compound with benzene, a yellow acetyl derivative is thus dissolved, and this, on hydrolysis with sulphuric acid in the presence of alcohol, yields a bright yellow colouring matter.†

Again, if carthamine is boiled with ammonium carbonate solution, a yellow liquid is obtained, which, when neutralised with acid, does not give a precipitate, and on evaporation to dryness gives an aurine-like mass, very soluble in water.

Aniline under suitable conditions also yields a yellow substance, which, however, in this case, is readily crystallised. Two grams of finely powdered carthamine, suspended in 25 c.c. of absolute alcohol, were treated with 25 drops of aniline, and the mixture digested at the boiling point for one hour. The carthamine gradually dissolved, and, on cooling, the orange-brown liquid gelatinised. Addition of boiling water caused, however, the formation of a clear solution, from which fine, yellow needles gradually separated, and after keeping overnight these were collected, washed with dilute alcohol with absolute alcohol, and finally with ether. For purification, the substance was dissolved in a little hot pyridine, the solution treated with twice its volume of boiling 50 per cent. alcohol, and the glistening, yellow needles, which separated on

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* When carthamine is acetylated in presence of zinc, a colourless acetyl derivative is obtained, which has yet only been isolated in an amorphous condition.

† An analysis of this compound is withheld until further confirmation is possible.

cooling, twice recrystallised in a similar manner. It then melted and decomposed at 276—278°. Finally, some portion of the compound was dissolved in boiling acetic acid by the aid of a few drops of water, the solution diluted with boiling water, and, when cold, the crystals collected and again recrystallised by this process. The latter treatment, however, proved to be unnecessary, for it was ascertained that no alteration in the decomposition point had been thus effected. The substance contained nitrogen, and the yield averaged about 30 per cent. of the carthamine employed. For analysis it was dried at 160°:

Found, $C = 61{\cdot}10$, $60{\cdot}71$, $60{\cdot}92$; $H = 4{\cdot}73$, $5{\cdot}05$, $5{\cdot}26$; $N = 2{\cdot}65$, $2{\cdot}72$.

$C_{25}H_{24}O_{12},C_6H_7N$ requires $C = 61{\cdot}08$; $H = 5{\cdot}09$; $N = 2{\cdot}29$ per cent.

This substance, which, on heating, develops a bright orange tint, and for which the name *aniline xanthocarthaminate* is proposed, can also be prepared by boiling carthamine in pyridine solution with a little aniline. During its preparation very little decomposition occurs; that is, in the sense of the formation of products soluble in ether.* It is almost insoluble in boiling alcohol, slightly more soluble in boiling acetic acid, and dissolves in alkaline solutions with a pale yellow colour. If the alkaline liquid is neutralised with hydrochloric acid in the cold, a gelatinous precipitate separates, which, when collected and washed with water, gradually dissolves, but if the acidified mixture is kept for some time or is gently warmed, the precipitate becomes more granular, is then insoluble in water, and has the decomposition point of the original substance. In a second experiment employing 10 per cent. potassium hydroxide solution, the solution was kept for some time, and the precipitate produced from it by acetic acid, crystallised from dilute alcoholic pyridine and submitted to analysis:

Found, $C = 60{\cdot}77$; $H = 5{\cdot}09$ per cent.

It decomposed at 273—274°, and was evidently the original compound. By boiling with acetic anhydride, it slowly dissolves, but decomposition gradually occurs, and the solution becomes olive-coloured.

For the purpose of obtaining further information as to the molecular weight of this compound, the β-naphthylamine derivative was prepared by boiling a mixture of 2 grams of carthamine, 1·5 grams of β-naphthylamine, and 30 c.c. of alcohol for one hour. The product was treated with boiling water, and the crystals which separated on cooling were collected and allowed to drain on porous porcelain. When almost dry, the product was made into a thin cream with alcohol, the insoluble residue collected, washed with alcohol, and crystallised three times from dilute alcoholic pyridine. For analysis it was dried at 160°:

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* The dilute alcoholic mother liquid, when acidified and extracted with ether, gave a trace of a crystalline residue, which contained *p*-coumaric acid and a substance resembling *p*-hydroxybenzaldehyde.

Found, C = 63·47; H = 5·09; N = 2·18.

$C_{25}H_{24}O_{12},C_{10}H_9N$ requires C = 63·73; H = 5·01; N = 2·12 per cent.

β-Naphthylamine xanthocarthaminate forms beautiful orange-coloured leaflets, which, when heated, become bright scarlet-coloured, sinter at about 260°, and melt and decompose at about 266—268°. It dissolves in alkaline solutions with a pure yellow colour, and after some time a precipitate separates, which has the properties of β-naphthylamine. ψ-Cumidine also reacts with carthamine, giving a product crystallising in glistening, orange-coloured leaflets, which sintered at 285°, and melted and decomposed at about 290°. When dissolved in alkaline solutions, the pale yellow liquid possesses the characteristic odour of ψ-cumidine, and gradually deposits crystals of this base. Attempts to prepare the *p*-chloroaniline derivative in a pure condition, and made with the object of obtaining a chlorine estimation, gave a gelatinous product, which was not readily crystallised.

As far as the evidence is therefore available, these compounds are probably the salts of an acid provisionally termed *xanthocarthaminic acid*. This compound, which would appear to be isomeric with carthamine, is closely allied to it, and preliminary experiments indicate as probable that it can be reconverted into this colouring matter in a simple manner.[*] Owing to lack of material, no serious attempt could be made to isolate the free acid, and such information which has been obtained as to this substance will be given after a fuller confirmation of its properties.

These yellow compounds indicate that the molecular weight of carthamine is high, being apparently represented by the formula $C_{25}H_{24}O_{12}$, and it was interesting to obtain further confirmation of this point by the preparation, if possible, of a potassium salt. When an alcoholic solution of carthamine is treated with potassium acetate, a colloidal precipitate of the potassium salt is formed, and to isolate this in a crystalline condition the following method was adopted. Finely powdered carthamine, suspended in boiling alcohol, is treated drop by drop with strong aqueous potassium acetate until a clear solution is produced. On cooling, crystals separate out, and these are collected, washed with absolute alcohol, then with ether, and dried at 160°:

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[*] When a cold solution of β-naphthylamine xanthocarthaminate is treated with alkali and, after keeping, is repeatedly extracted with ether to remove β-naphthylamine, the alkaline liquid when neutralised with hydrochloric acid gradually deposits a curdy, yellow precipitate. On keeping for some days, this slowly becomes red-coloured, and when dissolved in pyridine gives a red solution, closely resembling in tint that given by carthamine with the same solvent.

Found, K = 6·94, 7·28.

$C_{25}H_{23}O_{12}K$ requires K = 7·04 per cent.

This *potassium* salt consists of green, iridescent needles, and is decomposed with hot water with liberation of the free colouring matter. On this account an excess of water must not be added during its preparation.

In connexion with the molecular weight of carthamine, it was also interesting to determine the water of crystallisation in the pure air-dry material, evidence of the presence of which was shown by the hygroscopic nature of the anhydrous substance. In carrying out these experiments, the colouring matter was freed from pyridine by drying at 160°, was kept in air until its weight was constant, and the loss occasioned by heating it to 160° again determined:

Found, H_2O = 6·79, 6·57, 6·70.

$C_{25}H_{24}O_{12},2H_2O$ requires H_2O = 6·52 per cent.

Finally, experiments were carried out by the ebullioscopic method to ascertain the molecular weight of carthamine, employing methyl alcohol and pyridine as solvents, but without success, due in the first case to the limited solubility of the substance, and in the second apparently to slow decomposition at the boiling temperature. Application was therefore made to Dr. Barger, who very kindly consented to experiment on the subject by means of his microscopic method (Trans., 1904, **85**, 286), employing pyridine as a solvent. The results in three distinct experiments in which azobenzene was used for comparison were M.W. = 566, 537, and 551, whereas the formula $C_{25}H_{24}O_{12}$ requires M.W. = 516. These figures, taken in conjunction with the analytical numbers given by the aniline and β-naphthylamine xanthocarthaminates, the determinations of water of crystallisation, and the somewhat less trustworthy evidence given by the potassium salt, indicate that the formula of carthamine is, or closely approximates to $C_{25}H_{24}O_{12}$. The fact that carthamine, when hydrolysed with alkali, has given only *p*-coumaric acid and *p*-hydroxybenzaldehyde is peculiar in view of the fact that this compound contains so much oxygen, and that its benzoyl derivative indicates the presence of six or seven hydroxyl groups. In view of the numerous experiments which have been made on this point, it is hardly likely that a phenol is also produced during this decomposition, although a final experiment, employing some quantity of the dye, will, it is hoped, be carried out at a later date. The recent work of Dimroth on carminic acid (*Ber.*, 1909, **32**, 1611) and kermesic acid (*ibid.*, 1910, **33**, 1387) indicates that in addition to a naphthaquinone group, these dyestuffs contain a second nucleus, which is probably of an aliphatic nature, and it seems possible that in carthamine a group or groups of this character may exist.

It is unfortunate that at present no crystalline derivatives of carthamine have been prepared, but it is to be remembered, in regard to the very important colouring matter of logwood, hæmatein, the constitution of which is now clear, that such is also the case. The fact that carthamine so readily yields a yellow compound suggests that the yellow colouring matter of safflower may be connected with this reaction. This compound, which up to the present has only been isolated in the form of a syrup readily soluble in water, appears to contain a glucoside, and by digestion with boiling dilute sulphuric acid a small quantity of a crystalline, yellow substance has been isolated from it by means of ether. A further study of this product will be carried out as soon as the necessary raw material is available, and the continuation of this work on carthamine will shortly be resumed.

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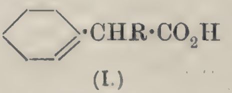
CXXXI.—Δ^3-p-*Menthenol*(8) *and* $\Delta^{3:8(9)}$-p-*Menthadiene.*

By William Henry Perkin, jun., and Otto Wallach.

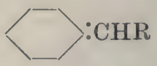
The difficulty of preparing substances belonging to the terpene group in a state of purity becomes more and more apparent as the chemistry of this group gradually develops, and this difficulty is most marked in the case of the terpenes themselves.

It is true that the presence even of considerable quantities of impurity does not always interfere with the characterisation of the substance in question. Thus, for example, α-terpinene ($\Delta^{1:3}$-*p*-dihydrocymene or $\Delta^{1:3}$-*p*-menthadiene) can be readily detected in mixtures by means of its nitrosite or by oxidation to αδ-dihydroxy-α-methyl-δ-*iso*propyladipic acid, although it has, so far, not been found possible to isolate the hydrocarbon in a pure state. It is also a comparatively simple matter to demonstrate the formation of dipentene during a reaction, although no method is known by which synthetical dipentene can be obtained quite free from isomerides or oxy-derivatives, such as cineol. On the other hand, small quantities of impurity interfere in a very serious way with the accurate measurement of physical properties, and it is, for this reason, often very difficult to determine with certainty the effect of slight changes in constitution on the physical properties of the terpenes. As an example of this, mention may be made of the widely differing values given by various investigators for the molecular refraction of α-terpinene, and of the difficulty which has been experienced of accurately determining the boiling point of dipentene. The preparation, in a pure condition, of alcohols and ketones of the terpene group does not usually present the difficulties which have so frequently been observed in the case of the terpenes themselves, because it is often possible to convert such alcohols or ketones into well-crystallised derivatives from which the parent substance may be regenerated, and the accurate determination of the physical constants of such alcohols or ketones is therefore a comparatively simple matter. In order to obtain a terpene in a pure state, it is best to prepare it synthetically, but, even in the case of syntheses which appear to proceed in a simple manner, there is always risk of intramolecular change, and recent investigations have emphasised the remarkable tendency exhibited by certain groupings in this respect.

In illustration of this, it is only necessary to call attention to the conversion of substances of the type (I) into hydrocarbons of the type (II), a change which has often been observed to take place



(I.)

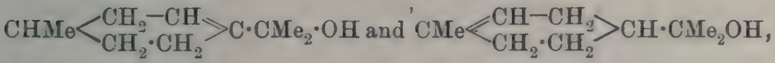


(II.)

during the elimination of carbon dioxide at comparatively low temperatures.

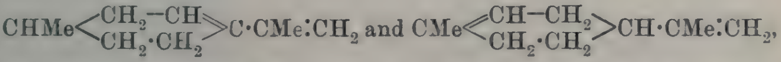
In order to be quite certain of the constitution of a given terpene, it is usually necessary to prepare it in several different ways, and it was with this object in view that we decided jointly to investigate certain terpenes and their derivatives, the accurate determination of the physical properties of which is of importance in connexion with the question of the effect exerted by double linkings in different positions. The present communication deals with Δ^3-*p*-menthenol(8) and $\Delta^{3:8(9)}$-*p*-menthadiene, substances which had already been prepared by W. H. Perkin, jun., and S. S. Pickles (Trans., 1905, **87**, 639), and contains a description of an entirely new method for the preparation of these substances discovered by O. Wallach.

Δ^3-*p*-Menthenol(8) differs from *α*-terpineol,



$$\mathrm{CHMe}\Big<\begin{matrix}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\Big>\mathrm{C{\cdot}CMe_2{\cdot}OH}\text{ and }\mathrm{CMe}\Big\lll\begin{matrix}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\Big>\mathrm{CH{\cdot}CMe_2OH},$$

in the position of the double linking, and $\Delta^{3:8(9)}$-*p*-menthadiene differs from limonene,

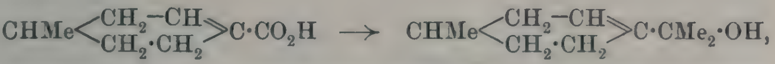


$$\mathrm{CHMe}\Big<\begin{matrix}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\Big>\mathrm{C{\cdot}CMe{:}CH_2}\text{ and }\mathrm{CMe}\Big\lll\begin{matrix}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\Big>\mathrm{CH{\cdot}CMe{:}CH_2},$$

not only in this respect, but also in the relation of the double linkings to one another.

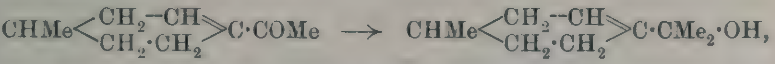
In the case of $\Delta^{3:8(9)}$-*p*-menthadiene, the two ethenoid linkings are conjugated, a condition of things which causes the molecular refraction of this substance to exhibit exaltation above that of limonene (compare Trans., 1906, **89**, 855).

Two methods are now available for the preparation of Δ^3-*p*-menthenol(8). Perkin and Pickles (*loc. cit.*) obtained this alcohol from the ester of Δ^3-tetrahydro-*p*-toluic acid (1-methyl-Δ^3-*cyclo*hexene-4-carboxylic acid) by the action of the Grignard reagent:



$$\mathrm{CHMe}\Big<\begin{matrix}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\Big>\mathrm{C{\cdot}CO_2H}\longrightarrow\mathrm{CHMe}\Big<\begin{matrix}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\Big>\mathrm{C{\cdot}CMe_2{\cdot}OH},$$

whereas Wallach (*Annalen*, 1909, **365**, 272) synthesised 4-acetyl-1-methyl-Δ^3-*cyclo*hexene, and then converted this substance into Δ^3-menthenol(8):

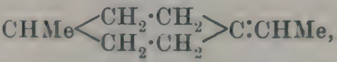


$$\mathrm{CHMe}\Big<\begin{matrix}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\Big>\mathrm{C{\cdot}COMe}\longrightarrow\mathrm{CHMe}\Big<\begin{matrix}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\Big>\mathrm{C{\cdot}CMe_2{\cdot}OH},$$

and an account of this method is given in the present communication.

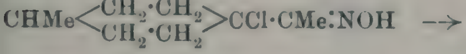
4-*Acetyl*-1-*methyl*-Δ^3-cyclo*hexene*.

In preparing this ketone, the semicyclic hydrocarbon, 1-methyl-4-ethylidene*cyclo*hexane,

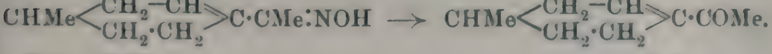


$$\mathrm{CHMe}\Big<\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\Big>\mathrm{C{:}CHMe},$$

is converted into the nitroso-chloride, and this, by elimination of hydrogen chloride, into the oxime, from which the ketone is obtained by hydrolysis:



$$\mathrm{CHMe}\Big<\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\Big>\mathrm{CCl{\cdot}CMe{:}NOH}\longrightarrow$$



$$\mathrm{CHMe}\Big<\begin{matrix}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\Big>\mathrm{C{\cdot}CMe{:}NOH}\longrightarrow\mathrm{CHMe}\Big<\begin{matrix}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\Big>\mathrm{C{\cdot}COMe}.$$

The fact that 1-methyl-4-ethylidene*cyclo*hexane may now be prepared in considerable quantities has made the investigation of several interesting stereo-isomeric derivatives possible. The nitroso-chloride, which is obtained in an excellent yield by the process already described, may be separated, by repeated crystallisation from acetone,* into two distinct substances. The more sparingly soluble component crystallises in needles, and melts at 117—118°, the more readily soluble isomeride crystallises in plates, and melts at 113—114°; both are volatile in steam. The higher melting substance yields, on careful treatment with piperidine, a nitrolpiperidide melting at 130—131°, and the same treatment converts the isomeride into a nitrolpiperidide which melts at 119—120°. Both crystallise from methyl alcohol in such similar forms that it is almost impossible to distinguish them by their appearance only. During the determination of the melting point of the nitrolpiperidide melting at 119—120°, the observation was made that the substance, after it had crystallised in the tube, melted at a higher temperature than before. When larger quantities were melted in a test-tube, a strong odour of piperidine was noticed, showing that partial decomposition into the oxime was taking place (compare Wallach, *Terpene und Campher*, p. 80).

The residue, after crystallisation, melted at 130—131°, showing that a conversion of the lower melting nitrolpiperidide into the isomeride of higher melting point had taken place. That these nitrolpiperidides are merely stereoisomeric and not chemically distinct is proved by the fact that both, on elimination of hydrogen chloride, yield the same oxime. In preparing the oxime of 4-acetyl-1-methyl-Δ^3-*cyclo*hexene, the crude nitroso-chloride may therefore be employed, and experience has shown that it is better to avoid the use of sodium methoxide for the elimination of the hydrogen chloride. In some cases this reagent has been found to be useful, but as a rule it is to be avoided because of the possibility of the formation of methoxy-derivatives from the nitroso-chloride by the exchange of chlorine for methoxyl (compare Deussen, *Annalen*, 1909, **369**, 62). Traces of such methoxy-derivatives are difficult to remove, and are apt to give rise to inaccurate observations of the properties of the oximes (compare *Annalen*, 1908, **359**, 303). In the present instance, the sodium acetate and acetic acid method was employed for the elimination of the hydrogen chloride with excellent results (Wallach, *Terpene und Campher*, p. 86), and, during the investigation of the products, the observation was made for the first time that a relatively stable intermediate acetyl derivative was produced according to the scheme:

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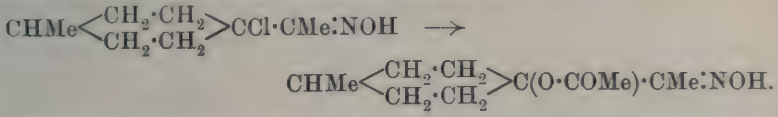
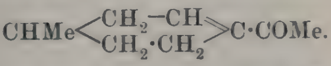
* For observations on the suitability of acetone for the crystallisation of nitroso-chlorides and similar derivatives, compare Wallach, *Terpene und Campher*, p. 65; and *Annalen*, 1904, **336**, 43.



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CCl\cdot CMe{:}NOH} \longrightarrow \mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C(O\cdot COMe)\cdot CMe{:}NOH}.$$

The acetate, which in this case is crystalline, is decomposed on distillation into acetic acid and the unsaturated oxime,



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2-CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C\cdot COMe}.$$

In preparing the oxime, it is best to distil the product of action of sodium acetate on the nitroso-chloride, first under diminished and then under the ordinary pressure; the product is then crystallised from methyl alcohol, when the oxime (m. p. 116—117°) is readily obtained pure.

If the acetate, which when quite pure crystallises in large, transparent crystals and melts at 111—112°, is not completely decomposed before the crystallisation of the oxime, crops of crystals separate from the mother liquor, which melt at about 85° and consist of a mixture of the oxime and the acetate. This mixture is much more soluble in methyl alcohol than the components, and can only be separated into these by tedious fractional crystallisation.

In preparing 4-acetyl-1-methyl-Δ^3-*cyclo*hexene, the pure oxime is decomposed by warming with dilute sulphuric acid, and subsequent distillation in a current of steam. The resulting ketone always contains traces of oxime which have escaped hydrolysis, and in this, as in all other similar cases, if the pure ketone is required, it is necessary to purify the crude product by converting it into the semicarbazone.

This derivative (m. p. 222°) is then decomposed by dilute sulphuric or oxalic acid, and the ketone purified by distillation under ordinary pressure. The properties of 4-acetyl-1-methyl-Δ^3-*cyclo*hexene are the following:

B. p. 210—211°, $d_{20} = 0{\cdot}942$, $n_D = 1{\cdot}4830$ at 20°.
$M = 41{\cdot}22$. Calculated for $C_9H_{14}O$ $M = 41{\cdot}84$.
0·1703 gave 0·4887 CO_2 and 0·1581 H_2O. $C = 78{\cdot}3$; $H = 10{\cdot}4$.
$C_9H_{14}O$ requires $C = 78{\cdot}2$; $H = 10{\cdot}2$ per cent.

At low temperatures the ketone solidifies to a crystalline mass, which melts again at about $-20°$; it is rather soluble in water, and has an odour resembling aniseed. 4-Acetyl-1-methyl-Δ^3-*cyclo*hexene is isomeric with 4-acetyl-1-methyl-Δ^1-*cyclo*hexene, which is obtained by the oxidation of β-terpineol (m. p. 32°), the isomerism being due merely to the position of the ethenoid linking. The following table gives an interesting comparison of the properties of the two isomerides:

	4-Acetyl-1-methyl-Δ^1-*cyclo*hexene.	4-Acetyl-1-methyl-Δ^3-*cyclo*hexene.
B. p.	205—206°	210—211°
d	0·940	0·942
n_D	1·4719	1·4830
M	41·10	41·84
M. p. of oxime	51°	116—117°
M. p. of semicarbazone	165°	222°

The differences in the physical properties of the two ketones are in agreement with the generalisation which K. Auwers and F. von der Heyden (*Ber.*, 1909, **42**, 2406) and others have deduced as the result of the examination of a large number of cases, and which is briefly as follows. Experience shows that, when a double linking in a position removed from the carbonyl group becomes conjugated with that group, there is an increase in the boiling point, density, and refractive index, and of these properties the increase in the refractive index is the most evident in the particular case under review.

Conversion of 4-Acetyl-1-methyl-Δ^3-cyclo*hexene into* Δ^3-p-*Menthenol*(8).

The conversion of the ketone into the tertiary alcohol was carried out under the following conditions. The ketone (20 grams) dissolved in dry ether (60 c.c.) was gradually added to a Grignard solution prepared from magnesium (6 grams), methyl iodide (36 grams), and ether (110 grams), and the whole heated for two hours on the water-bath. The product was decomposed with water, and distilled in a current of steam, the receiver being changed as soon as the ether had passed over. It was frequently noticed that the menthenol crystallised in the condenser and receiver, but traces of impurity are sufficient to prevent crystallisation, and, unless a crystal is introduced, the pure substance will sometimes remain for weeks without crystallising (compare p. 1435):

0·1560 gave 0·4462 CO_2 and 0·1632 H_2O. C=78·0; H=11·7.

$C_{10}H_{18}O$ requires C=77·8; H=11·7 per cent.

Δ^3-p-*Menthenol*(8) melts at 39—40°, and distils at 97°/14 mm., or at 205° under the ordinary pressure. It has a strong and very pleasant odour, resembling that of α-terpineol, and, in contact with acids, it very readily loses water with formation of $\Delta^{3:8(9)}$-*p*-menthadiene.

It exhibits in a marked degree the property of superfusion, a fact which much facilitates the determination of its physical constants. The following values were observed:

$$d_{18}=0{\cdot}921,\ n_D=1{\cdot}4769 \text{ at } 18^\circ.$$

$$M=47{\cdot}16. \quad \text{Calculated for } C_{10}H_{17}{\cdot}OH \quad M=47{\cdot}19.$$

Δ^3-*p*-Menthenol(8) does not yield a crystalline derivative on treatment with nitrosyl chloride, but it combines with phenylcarbimide, and the *phenylurethane*, $C_{10}H_{17}O{\cdot}CO{\cdot}NH{\cdot}C_6H_5$, after crystallisation from methyl alcohol, melts and decomposes at about 128°. The melting point varies, however, considerably according to the rapidity with which the substance is heated, and a rapid determination gives a melting point some degrees higher than 128°.

Preparation of Δ^3-p-*Menthenol*(8) *and* $\Delta^{3:8(9)}$-p-*Menthadiene from* p-*Toluic Acid.*

This synthesis was first carried out by Perkin and Pickles in 1905 (Trans., **87**, 639). The first step consists in the reduction of *p*-toluic acid to 1-methyl*cyclo*hexane-4-carboxylic acid (hexahydro-*p*-toluic acid) by treatment in boiling *iso*amyl-alcoholic solution with a large excess of sodium. Since this process is very laborious and unpleasant, a series of experiments was made with the object of determining whether the reduction might not be effected in ethyl-alcoholic solution, but without result. Even when alcohol which had been twice distilled over calcium was employed (compare Trans., 1909, **95**, 1876, footnote), and the process carried out as vigorously as possible, no appreciable reduction took place. The whole of the material required for this investigation had, therefore, to be prepared by the original method (*loc. cit.*, p. 643), but certain modifications were introduced with advantage. The crude hexahydro-acid, obtained on acidifying the product of reduction, was distilled in a current of steam, and thus separated from resinous matter, when, in most cases, it was found that the colourless acid collected from the distillate, after crystallising from dilute acetic acid, melted at 112°, and was quite pure. If this was not the case, it was treated in alkaline solution with a little permanganate in the usual manner. The bromination of the pure 1-methyl*cyclo*hexane-4-carboxylic acid was carried out exactly as previously described (*loc. cit.*, p. 645), and the product poured into excess of alcohol and thus converted into ethyl 1-bromomethyl*cyclo*hexane-4-carboxylate (ethyl α-bromohexahydro-*p*-toluate). In the original experiments the elimination of hydrogen bromide from this ester was brought about by boiling alcoholic potassium hydroxide, but it is better to digest the crude ester with four times its volume of diethylaniline for two hours in a reflux apparatus.

The product is treated with excess of dilute hydrochloric acid, extracted with ether, the ethereal solution washed with dilute hydrochloric acid, dried, evaporated, and the ester distilled under diminished pressure, when almost the whole quantity distils at 148—152°/100 mm., the yield being nearly quantitative. The ethyl 1-methyl-Δ^1-*cyclo*hexene-4-carboxylate (ethyl Δ^1-tetrahydro-*p*-toluate) thus obtained was hydrolysed by methyl-alcoholic potassium hydroxide, and the acid twice crystallised from dilute acetic acid, when it melted at 134°, and was quite pure. This acid (40 grams) was next digested with alcohol (250 c.c.) and sulphuric acid (20 c.c.) for two hours, and the ester, after isolating in the usual manner, distilled at 152—153°/100 mm. (Found, $C=71{\cdot}4$; $H=9{\cdot}6$. Calc., $C=71{\cdot}4$; $H=9{\cdot}5$ per cent.)

On the former occasion (*loc. cit.*, p. 647) it was observed that this ester, when treated with magnesium methyl iodide, did not behave normally, since it was largely converted directly into $\Delta^{3:8(9)}$-*p*-menthadiene, the yield of Δ^3-*p*-menthenol(8) being very small.

In order, if possible, to avoid this dehydration, the ester (20 grams), diluted with five times its volume of ether, was cooled in ice and salt, and the ethereal solution of the magnesium methyl iodide (containing 8 grams of magnesium) gradually added. After being kept in the freezing mixture for four hours, the product was left overnight at the ordinary temperature, and then decomposed with water and dilute hydrochloric acid in the usual manner. The resulting oil was mixed with methyl-alcoholic potassium hydroxide ($KOH=5$ grams), and allowed to remain for twenty-four hours in order to remove any trace of unchanged ethyl 1-methyl-Δ^1-*cyclo*hexene-4-carboxylate. Water was then added, the neutral oil extracted with ether and distilled in a current of steam, the distillate was again extracted with ether, the ethereal solution dried carefully, and fractionated under diminished pressure, when about three-fourths distilled at 90—95°/30 mm., and consisted almost entirely of $\Delta^{3:8(9)}$-*p*-menthadiene, elimination of water having taken place in spite of the precautions which had been observed. The remainder, on repeated fractionation, yielded a pure specimen of Δ^3-*p*-menthenol(8), which distilled at 108—110°/30 mm., and crystallised at once when a crystal of the pure menthenol was introduced into the well-cooled oil. The mass was left in contact with porous porcelain until quite free from traces of oily impurity and then analysed. (Found, $C=77{\cdot}8$; $H=11{\cdot}8$. Calc., $C=77{\cdot}9$; $H=11{\cdot}7$ per cent.)

Δ^3-*p*-Menthenol(8) melts at 40—41°, and exhibits in a remarkable manner the phenomenon of superfusion (compare Trans., 1906, **89**, 851). Some of the pure substance was melted in a small sealed tube and left in the ice chest for three weeks, and, although it was repeatedly shaken, it could not be made to crystallise.

The tube was sent by post from Manchester to Göttingen in the winter time, and the substance arrived still fluid, but when a crystal was introduced the whole solidified at once to a hard, crystalline mass.

The *phenylurethane*, prepared in the usual manner, separated from dilute methyl alcohol in colourless needles, and melted, when rapidly heated, at 133—134° with decomposition. If, however, the determination was carried out slowly, the observed melting point was a few degrees lower:

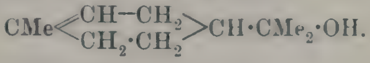
0·1411 gave 6·1 c.c. N_2 at 15° and 758 mm. N = 5·2.

$C_{17}H_{23}O_2N$ requires N = 5·1 per cent.

This preparation was mixed with an equal quantity of a specimen of the phenylurethane which had been prepared from Δ^3-*p*-menthenol(8) from 4-acetyl-1-methyl-Δ^3-*cyclo*hexene (p. 1432), and the mixture melted at the same temperature as the components.

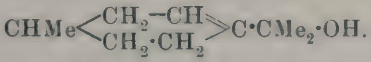
In connexion with the study of the influence of the position of the ethenoid linking on physical properties, it is very interesting to make a comparison of the physical properties of the known *p*-menthenols, namely:

I. Δ^1-*p*-Menthenol(8), or *α*-terpineol,



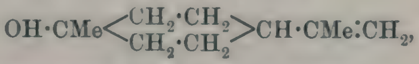
$$\mathrm{CMe}\left<\begin{matrix}\mathrm{CH{-}CH_2}\\\mathrm{CH_2{\cdot}CH_2}\end{matrix}\right>\mathrm{CH{\cdot}CMe_2{\cdot}OH.}$$

II. Δ^3-*p*-Menthenol(8),



$$\mathrm{CHMe}\left<\begin{matrix}\mathrm{CH_2{-}CH{=}}\\\mathrm{CH_2{\cdot}CH_2}\end{matrix}\right>\mathrm{C{\cdot}CMe_2{\cdot}OH.}$$

III. $\Delta^{8(9)}$-*p*-Menthenol(1), or *β*-terpineol,



$$\mathrm{OH{\cdot}CMe}\left<\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\\mathrm{CH_2{\cdot}CH_2}\end{matrix}\right>\mathrm{CH{\cdot}CMe{:}CH_2,}$$

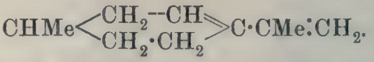
and we therefore append the following table:

	I.	II.	III.
Boiling point	218°	205°	209—210°
Melting ,,	35°	39°	32°
d_{20}	0·938	0·921	0·919
n_D	1·4820	1·4764	1·4749
Melting point of the phenylurethane	113°	128°	85°

The examination of these values discloses a remarkable relationship, since it is evident in this case that the approach of the ethenoid linking to the oxygen group causes a fall in boiling point, density, and refractive index, whereas the melting point rises.

In the case of the two ketones compared on p. 1432, exactly the reverse was shown to be the case. Further experiments are necessary in order to show whether this relationship holds good in other series, and whether it will be possible to draw valid conclusions as to constitution from comparisons such as these.

$\Delta^{3:8(9)}$-p-*Menthadiene*,



$$\mathrm{CHMe}\Big<\begin{matrix}\mathrm{CH_2{-}{-}CH}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\Big>\mathrm{C{\cdot}CMe{:}CH_2}.$$

It has already been mentioned that Δ^3-*p*-menthenol(8) loses the elements of water with great ease, and not only is this the case when it is treated with dehydrating agents, such as potassium hydrogen sulphate, but also when it is left in contact with dilute acids under conditions which, in the case of terpineol, bring about addition of water and formation of terpin. Thus, when the substance is shaken mechanically with 1 per cent. sulphuric acid for several days or warmed at 80° with 5 per cent. aqueous oxalic acid, it loses water with the formation of $\Delta^{3:8(9)}$-*p*-menthadiene. A specimen of the hydrocarbon, prepared by the latter process, was purified by distillation in a current of steam and subsequent repeated fractionation over sodium, and analysed:

0·1202 gave 0·3882 CO_2 and 0·1314 H_2O. C = 88·1; H = 12·2.

$C_{10}H_{16}$ requires C = 88·1; H = 11·9 per cent.

$\Delta^{3:8(9)}$-*p*-Menthadiene has an odour which can scarcely be distinguished from that of limonene, and the determination of its physical properties gave the following values:

B. p. 184—185°, $d_{19} = 0{\cdot}858$, $n_D = 1{\cdot}4924$ at 19°.

M = 46·02. Calculated for $C_{10}H_{16}|^{=2}$ M = 45·24.

It does not yield crystalline derivatives on treatment with halogen acids, nitrosyl chloride, or oxides of nitrogen (compare Perkin and Pickles, Trans., 1906, **89**, 648). The constitution of the terpene was controlled by oxidation with 1 per cent. permanganate at 0°, when a solid acid was obtained which, after crystallisation from a mixture of benzene and light petroleum, melted at 94—96°. The silver salt was analysed. (Found, Ag = 57·5. $C_7H_{10}O_4Ag$ requires Ag = 57·8 per cent.)

There can be no doubt that this acid was β-methyladipic acid, and its formation is in harmony with the position of the double linking in $\Delta^{3:8(9)}$-*p*-menthadiene, since, if the double linking were in any other position, or if both double linkings were in the ring, β-methyladipic acid could not have been produced on oxidation.

The examination of the physical constants given above shows at once that the terpene produced by the dehydration of Δ^3-*p*-menthenol(8) by treatment with 5 per cent. aqueous oxalic acid exhibits a remarkably high boiling point, density, and refractive index, and these high constants are readily explained by the assumption that the molecule contains conjugated ethenoid linkings.

Kay and Perkin (Trans., 1906, **89**, 849) had previously prepared *d*-$\Delta^{3:8(9)}$-*p*-menthadiene from *d*-Δ^3-*p*-menthenol(8) by warming with magnesium methyl iodide, and this active terpene exhibited the same properties as the inactive specimen just mentioned, namely, b. p. 184°/748 mm., $d_{25}=0·8574$, and $M=46·0$. On the other hand, the inactive *p*-menthadiene prepared by Perkin and Pickles (Trans., 1905, **87**, 639), while boiling at the same temperature, had the low density, $d_{20}=0·8358$. The amount of inactive terpene available at that time was very small, and there is therefore every reason to suppose that the low density was due to the presence of small quantities of impurity. Since, however, the accurate determination of the physical constants in this case is of particular importance, the synthesis of the hydrocarbon by the laborious method employed by Perkin and Pickles (*loc. cit.*) was undertaken on a much larger scale than before, and resulted in the preparation of no less than 50 grams of inactive $\Delta^{3:8(9)}$-*p*-menthadiene. This hydrocarbon, after purification by distillation in a current of steam and repeated fractionation over sodium, yielded the following analysis and physical constants:

0·1913 gave 0·6169 CO_2 and 0·2038 H_2O. $C=87·9$; $H=11·8$.

$C_{10}H_{16}$ requires $C=88·1$; $H=11·9$ per cent.

B. p. 184—188°, $d_{20}=0·8600$, $n_D=1·4915$ at 20°, $M=54·84$.

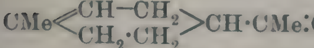
The comparison of the physical properties of the two specimens of $\Delta^{3:8(9)}$-*p*-menthadiene prepared (I) from 4-acetyl-1-methyl-Δ^3-*cyclo*hexene and (II) from 1-methyl-Δ^1-*cyclo*hexene-4-carboxylic acid exhibits such a close agreement that there can be little doubt that this terpene is now correctly characterised.

	B. p.	*d*.	n_D.	M.
I.	184—185°	0·858	1·4924	46·02
II.	184—186	0·860	1·4915	45·84
			Calculated for $C_{10}H_{16}|^{=}_{2}$	45·24

Limonene, on the other hand, has

B. p.	*d*.	n_D.	M.
175—176°	0·846	1·4746	45·23

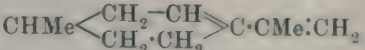
When the formulæ of the two hydrocarbons:



$$\mathrm{CMe}\Big<\begin{matrix}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\Big>\mathrm{CH{\cdot}CMe{:}CH_2}$$

Limonene.

and



$$\mathrm{CHMe}\Big<\begin{matrix}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\Big>\mathrm{C{\cdot}CMe{:}CH_2}$$

$\Delta^{3:8(9)}$-*p*-Menthadiene.

are compared, it is evident that the approach of the ethenoid linkings to the conjugated position has resulted in a very considerable rise in boiling point, density, and refractive index, and this change in the constants is of the same order as that shown by the ketones (p. 1432), but the reverse of that exhibited by the alcohols (p. 1435).

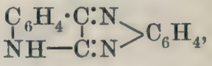
The facts which we have established in this research seem to suggest an explanation for the observation which has so often been made that, in the synthetical preparation of dipentene, substances are always produced which boil higher than that hydrocarbon, and yet are not terpinolenes. It is possible that the reagents employed may cause partial intramolecular change to take place, and that the ethenoid linking in the ring may wander from the Δ^1- to the Δ^3-position. This point might be decided by the investigation of the amount of bromine absorbed by the higher fractions obtained during the preparation of dipentene, since Perkin and Pickles (Trans., 1905, **87**, 641) have shown that $\Delta^{3:8(9)}$-*p*-menthadiene, owing to its containing conjugated ethenoid linkings, is only capable of absorbing two atoms of bromine, whereas dipentene, under the same conditions, yields dipentene tetrabromide.

MANCHESTER AND GÖTTINGEN.

CXXXII.—*Cyclic Di- and Tri-ketones.*

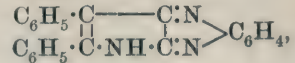
By SIEGFRIED RUHEMANN.

THE close resemblance between isatin and the diketopyrrolines, which has been pointed out previously (Trans., 1909, **95**, 984, 1603; 1910, **97**, 462), exists also in the behaviour of these substances towards *o*-phenylenediamine. In the same way as this diamine condenses with isatin to indophenazine,



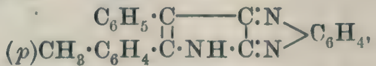
$$\left.\begin{array}{l} C_6H_4\cdot C{:}N \\ NH{-}C{:}N \end{array}\right>C_6H_4,$$

it yields similar compounds with the diketopyrrolines. I have prepared, thus, *diphenylpyrrolinophenazine*,



$$\left.\begin{array}{l} C_6H_5\cdot C{=\!=}C{:}N \\ C_6H_5\cdot C\cdot NH\cdot C{:}N \end{array}\right>C_6H_4,$$

and *phenyl*-p-*tolylpyrrolinophenazine*,



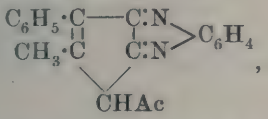
$$\left.\begin{array}{r} C_6H_5\cdot C{=\!=}C{:}N \\ (p)CH_3\cdot C_6H_4\cdot C\cdot NH\cdot C{:}N \end{array}\right>C_6H_4,$$

which substances, like indophenazine, are yellow.

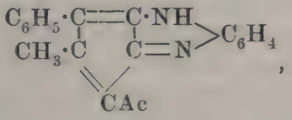
The red diketo*cyclo*pentene derivative, $C_{14}H_{12}O_3$, which is formed from the product of the action of sodioacetylacetone on phenylpropiolyl chloride (Ruhemann and Merriman, Trans., 1905, **87**, 1383) also condenses with the diamine thus:

$$C_{14}H_{12}O_3 + C_6H_4(NH_2)_2 = C_{20}H_{16}ON_2 + 2H_2O;$$

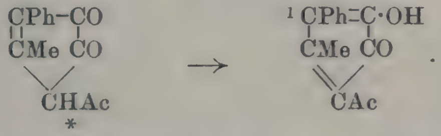
but the compound which is produced differs in colour from the phenazines, since it is purple. This fact leads to the conclusion that it has not the constitution:



but



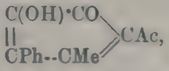
and that its formation is preceded by the change of diketoacetylphenylmethyl*cyclo*pentene into its tautomeric form:



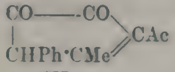
This view as to the formula of the purple condensation product, which is indicated by the similarity of its colour with that of the salts of the diketo*cyclo*pentene derivative, $C_{14}H_{12}O_3$, is supported by the following considerations. The hydrogen, marked by an

---

[1] An error occurs in my paper, "Condensation of Amides with Esters of Acetylenic Acids" (Trans., 1909, **95**, 984), which requires correction. Whereas the tautomeric form of the *cyclo*pentene derivative, $C_{14}H_{12}O_3$, is correctly represented thus:

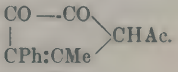


the formula of the compound with the diketonic grouping (p. 986) is erroneously given as:



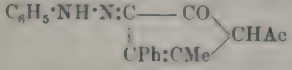
(VI.)

instead of

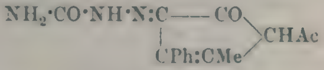


(VI.)

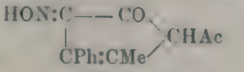
After having established the nature of the tautomeric change of this substance by a comparison of its properties with isatin and the diketopyrrolines (*loc. cit.*), another correction becomes imperative. This concerns the formulæ of some of the derivatives of the diketone, $C_{14}H_{12}O_3$, which were described previously (Trans., 1906, **89**, 682). The formulæ given there must be changed to:



The phenylhydrazone.

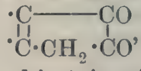


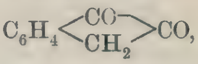
The semicarbazone.



The oxime of diketophenylmethylacetyl*cyclo*pentene.

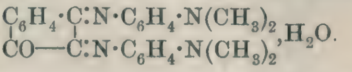
asterisk, has a greater mobility than the iminic hydrogen of isatin or the diketopyrrolines. Whereas the latter substances, with alkalis only, yield blue solutions which quickly change to yellow, the diketo*cyclo*pentene derivative, $C_{14}H_{12}O_3$, dissolves not only in alkalis, but also in alkali carbonates or acetates, to form blue salts, and these are considerably more stable than the salts of the former diketone. Again, the diketopyrrolines do not give blue solutions on the addition of piperidine, but form with it colourless additive products (this vol., p. 465); the diketo*cyclo*pentene derivative, $C_{14}H_{12}O_3$, on the other hand, dissolves in piperidine, as it does in alkalis or alkali carbonates, to yield a blue solution. It follows therefore that this diketone readily undergoes a transformation into its tautomeric form, which occurs, also, in its condensation with *o*-phenylenediamine. Reagents, like phenylhydrazine or hydroxylamine, do not effect this change, but form with the diketone a phenylhydrazone or an oxime (Ruhemann, Trans., 1906, **89**, 682). Nor does such a transformation occur in the reaction of phenylmercaptan with the diketone, which yields an additive product; this, in every respect, resembles the one which is formed by the union of the mercaptan with diketodiphenylpyrroline (*loc. cit.*).

On the one hand, the similarity, on the other the difference, which exists between the diketo*cyclo*pentene derivative, $C_{14}H_{12}O_3$, and isatin, or the diketopyrrolines, induced me to attempt the preparation of diketopentenes with the grouping  $\begin{array}{l}\cdot C\text{——}CO\\ \cdot C\cdot CH_2\cdot CO\end{array}$, in which the methylene radicle is intact. With this object in view, as well as for the purpose of arriving at a compound which in constitution closely resembles isatin, I chose α-hydrindone as starting point. I expected that this substance, by means of Sachs and Barschall's method of changing methylene groups into ketonic groups (*Ber.*, 1901, **34**, 3047), would be transformed into 1:2-diketohydrindene,



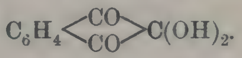
$$C_6H_4<\begin{array}{l}CO\text{—}\\ CH_2\end{array}>CO,$$

the isomeride of the known 1:3-diketohydrindene. The experiment, however, led to the remarkable result that, in the presence of potassium hydroxide or sodium carbonate, *p*-nitrosodimethylaniline mainly attacks both methylene groups of α-hydrindone. Analysis of the substance which is formed points to the formula $C_{25}H_{24}ON_4,H_2O$; accordingly, it is to be represented thus:



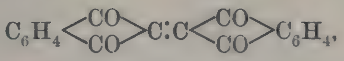
$$\begin{array}{l}C_6H_4\cdot C{:}N\cdot C_6H_4\cdot N(CH_3)_2\\ CO\text{—}C{:}N\cdot C_6H_4\cdot N(CH_3)_2\end{array},H_2O.$$

That, indeed, nitrosodimethylaniline has entered into both methylene groups of the hydrindone follows from the behaviour of mineral acids towards the condensation product; thus, it is readily decomposed, and yields the *hydrate* of *triketohydrindene*.



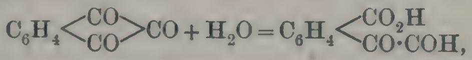
$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C(OH)_2.$$

Some years ago Kaufmann (*Ber.*, 1897, **30**, 387) stated that he obtained triketohydrindene, along with diphthalylethylene (indenigo),



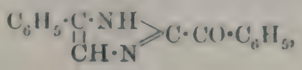
$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C{:}C<\begin{matrix}CO\\CO\end{matrix}>C_6H_4,$$

on oxidation of 1:3-diketohydrindene by means of hydrogen peroxide, but that the amount which was formed did not suffice for analysis. He described his compound as crystallising from glacial acetic acid in yellowish-brown plates, which were insoluble in alkalis, and decomposed at 190—206°. The substance which is produced from α-hydrindone has quite different properties, and these fully characterise it as triketohydrindene. It crystallises from water or alcohol in the form of its colourless hydrate, which, on heating, first loses water and turns red, then melts, and decomposes at 239—240°. The triketone readily reduces Fehling's solution and ammoniacal silver solutions. This fact is undoubtedly due to the opening up of the five-carbon ring and the formation of the semialdehyde of phthalonic acid, namely, phenylglyoxal-*o*-carboxylic acid, thus:



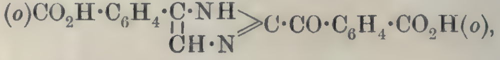
$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>CO+H_2O=C_6H_4<\begin{matrix}CO_2H\\CO\cdot COH,\end{matrix}$$

which is finally oxidised to phthalonic acid. Of especial interest is the action of ammonia on the triketone. If the aqueous solution of the mixture of both substances is kept for a short time, it turns a deep reddish-violet, and no longer reduces silver nitrate. On the addition of dilute hydrochloric acid, a red solid is precipitated, which has the empirical formula $C_9H_5O_2N$. This formula, undoubtedly, should be doubled. The constitution of the substance may be deduced from a consideration of the action of ammonia on phenylglyoxal, $C_6H_4\cdot CO\cdot COH$. Müller and v. Pechmann (*Ber.*, 1889, **22**, 2557), who studied this reaction, did not arrive at the correct empirical formula of the compound which is formed. This was established by Pinner (*Ber.*, 1902, **35**, 4134), who showed, also, that the substance was identical with the one which Engler and Hassenkamp (*Ber.*, 1885, **18**, 2241) obtained on treatment of dibromoacetophenone with ammonia. Pinner, further, considered that it is to be represented thus:



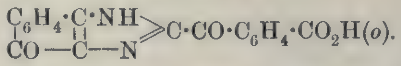
$$\begin{array}{l}C_6H_5\cdot C\cdot NH\\ \qquad\;\;\|\\ \qquad\;CH\cdot N\end{array}\!\!>C\cdot CO\cdot C_6H_5,$$

and accordingly to be regarded as 2-benzoyl-5-phenylglyoxaline. Since the reducing action of triketohydrindene can only be explained by the opening up of the five-carbon ring and the formation of phenylglyoxal-*o*-carboxylic acid, the action of ammonia may be explained, as in the case of phenylglyoxal, by the assumption that the aldehydo-acid, first, condenses to the dicarboxylic acid,



$$(o)\mathrm{CO_2H\cdot C_6H_4\cdot}\begin{array}{l}\mathrm{C\cdot NH}\\ \| \\ \mathrm{CH\cdot N}\end{array}\!\!\geqslant\mathrm{C\cdot CO\cdot C_6H_4\cdot CO_2H}(o),$$

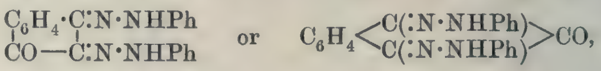
which subsequently loses water and yields:



$$\begin{array}{l}\mathrm{C_6H_4\cdot C\cdot NH}\\ |\qquad\;\; \| \\ \mathrm{CO - C - N}\end{array}\!\!\geqslant\mathrm{C\cdot CO\cdot C_6H_4\cdot CO_2H}(o).$$

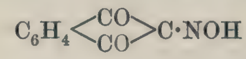
The product thus appears both to contain the indone ring and to be a derivative of glyoxaline. It may therefore be called 2-o-*carboxybenzoylindonoglyoxaline*. Experiments to prove the correctness of this view are in progress.

Triketohydrindene condenses with phenylhydrazine to an orange-coloured diphenylhydrazone, the constitution of which is either



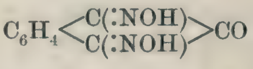
$$\begin{array}{l}\mathrm{C_6H_4\cdot C\colon N\cdot NHPh}\\ |\qquad\;\; | \\ \mathrm{CO - C\colon N\cdot NHPh}\end{array}\quad\text{or}\quad \mathrm{C_6H_4}\!<\!\begin{array}{l}\mathrm{C(\colon N\cdot NHPh)}\\ \mathrm{C(\colon N\cdot NHPh)}\end{array}\!>\!\mathrm{CO},$$

I am inclined to regard the first formula as correct; a similar formula would represent the yellow disemicarbazone, $C_9H_4O(\colon N\cdot NH\cdot CO\cdot NH_2)_2$, which triketohydrindene forms with semicarbazide. The formation of a trihydrazone or trisemicarbazone does not take place; hydroxylamine, however, is capable of producing a trioxime. Oximes of triketohydrindene are already known, namely, 2-oximino-1 : 3-diketohydrindene,



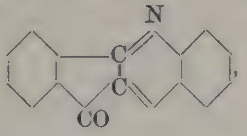
$$\mathrm{C_6H_4}\!<\!\begin{array}{l}\mathrm{CO}\\ \mathrm{CO}\end{array}\!>\!\mathrm{C\cdot NOH}$$

(Wislicenus, *Annalen*, 1888, **246**, 347); further, 1 : 3-dioximino-2-hydrindone,



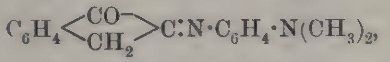
$$\mathrm{C_6H_4}\!<\!\begin{array}{l}\mathrm{C(\colon NOH)}\\ \mathrm{C(\colon NOH)}\end{array}\!>\!\mathrm{CO}$$

(Heusler and Schieffer, *Ber.*, 1899, **32**, 32), and finally trioximinohydrindene, $C_9H_4(\colon NOH)_3$, which Wislicenus and Koetzle (*Annalen*, 1889, **252**, 74) prepared by treating 2-oximino-1 : 3-diketohydrindene with hydroxylamine. The latter substance is the chief product contained in the mixture of oximes which is formed by the action of hydroxylamine on triketohydrindene. Although I have been unable to isolate the trioxime in the pure state, its formation is sufficiently established by the analytical result of the mixture. Triketohydrindene condenses with *o*-phenylenediamine to **ketohydrindenophenazine**,



which is yellow.

The behaviour of *p*-nitrosodimethylaniline towards *α*-hydrindone induced me to ascertain whether, besides the compound $C_{25}H_{26}O_2N_4$, the dimethylaminoanil,

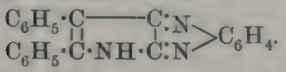


$$C_6H_4<\begin{matrix}CO\\CH_2\end{matrix}>C{:}N\cdot C_6H_4\cdot N(CH_3)_2,$$

is formed in the reaction. On examining the mother liquor from the black solid, $C_{25}H_{26}O_2N_4$, which separates if the alcoholic solution of the mixture of *p*-nitrosodimethylaniline and *α*-hydrindone is treated with potassium hydroxide, I found that, in the course of a few days, it deposited a red solid, which separated from alcohol in beautiful red crystals, but the yield was so small that it sufficed only for an analysis. Although the analytical data are not in full agreement with the theory, they indicate that the substance is indeed the dimethylaminoanil of *α*-hydrindone.

EXPERIMENTAL.

Diphenylpyrrolinophenazine,



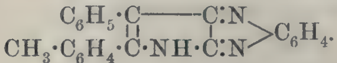
$$\begin{matrix}C_6H_5\cdot C & \text{——} & C{:}N\\ \| & & \vert \\ C_6H_5\cdot C & \cdot NH\cdot & C{:}N\end{matrix}>C_6H_4.$$

This compound separates as a yellow solid when the mixture of diketodiphenylpyrroline and *o*-phenylenediamine, dissolved in dilute acetic acid, is digested on the water-bath. It is sparingly soluble in cold, moderately so in boiling, alcohol, and crystallises in yellow needles, which melt at 240—241°:

0·1750 gave 0·5272 CO_2 and 0·0765 H_2O. C = 82·16; H = 4·86.
0·1855 ,, 20·8 c.c. N_2 at 15° and 759 mm. N = 13·11.
$C_{22}H_{15}N_3$ requires C = 82·24; H = 4·67; N = 13·08 per cent.

The substance dissolves in cold concentrated sulphuric acid, yielding a solution which is purple in transmitted, green in reflected, light; the solution in hydrochloric acid is red.

*Phenyl-*p*-tolylpyrrolinophenazine,*



$$\begin{array}{l} C_6H_5\cdot C\text{———}C{:}N \\ \quad\quad\;\; \| \qquad\quad\;\; | \\ CH_3\cdot C_6H_4\cdot C\cdot NH\cdot C{:}N \end{array}\!\!>C_6H_4.$$

This is prepared from diketophenyl-*p*-tolylpyrroline and *o*-phenylenediamine in the same way as the former substance, with the only exception that a more concentrated solution of acetic acid must be used on account of the fact that this diketone is less soluble than diketodiphenylpyrroline. The phenazine is moderately soluble in boiling alcohol, and, on cooling the solution, slowly separates in yellow needles, which melt at 258°:

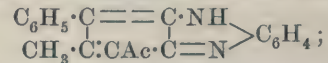
0·1833 gave 0·5532 CO_2 and 0·0865 H_2O. C = 82·30; H = 5·24.
0·1788 „ 19·4 c.c. N_2 at 17° and 762 mm. N = 12·62.
$C_{23}H_{17}N_3$ requires C = 82·38; H = 5·07; N = 12·54 per cent.

Action of o-*Phenylenediamine on* 2: 3-*Diketo*-1-*acetyl*-4-*phenyl*-5-*methyl*cyclo*pentene.*

On adding to the red diketo*cyclo*pentene derivative, $C_{14}H_{12}O_3$ (1 gram), dissolved in hot alcohol or acetic acid, *o*-phenylenediamine (0·5 gram), the whole sets to a mass of dark-coloured crystals. The product of the reaction is almost insoluble in alcohol, but dissolves in boiling glacial acetic acid, from which it crystallises in bunches of purple needles, softening at 245° and melting at 250°:

0·1782 gave 0·5225 CO_2 and 0·0855 H_2O. C = 79·97; H = 5·33.
0·1720 „ 14·2 c.c. N_2 at 21° and 747 mm. N = 9·23.
$C_{20}H_{16}ON_2$ requires C = 80·00; H = 5·33; N = 9·33 per cent.

The substance dissolves in cold concentrated sulphuric or hydrochloric acids to yield purple solutions. It has been pointed out before (p. 1439) that this compound must be represented thus:



$$\begin{array}{l} C_6H_5\cdot C\!=\!=\!C\cdot NH \\ \quad\quad\;\; | \qquad\;\;\; | \\ CH_3\cdot C{:}CAc\cdot C\!=\!N \end{array}\!\!>C_6H_4;$$

it may be called iso*phenylmethylacetyl*cyclo*pentenephenazine.*

With phenylmercaptan, the diketo*cyclo*pentene derivative, $C_{14}H_{12}O_3$, unites to yield the additive compound, $C_{14}H_{12}O_3,C_6H_6S$. This is formed when the diketone (0·5 gram), dissolved in hot alcohol, is mixed with phenylmercaptan (0·3 gram). The red colour of the solution changes to yellow, and, on adding water until turbidity is produced, yellow prisms separate, which soften at 125° and melt at 130° to a red liquid:

0·2344 (dried in a vacuum) gave 0·1650 $BaSO_4$. S = 9·67.
$C_{20}H_{18}O_3S$ requires S = 9·47 per cent.

This compound, like the product of the union of diketodiphenylpyrroline with phenylmercaptan, readily decomposes into its constituents, the diketone and the mercaptan.

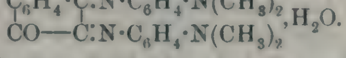
Action of p-*Nitrosodimethylaniline on α-Hydrindone.*

α-Hydrindone was prepared by the action of aluminium chloride on phenylpropionyl chloride, according to the method elaborated by Kipping (Trans., 1894, **65**, 484), and the yield was found to be the same as stated by this author, if his directions are closely followed. The action of nitrosodimethylaniline on the hydrindone takes place under the influence of alcoholic potassium hydroxide, and is accompanied by development of heat. After several experiments, the following mode of procedure was adopted as giving the best results. The hydrindone (6 grams) and nitrosodimethylaniline (24 grams), dissolved in equal volumes of alcohol (about 50 c.c.), are mixed, the solution is cooled by ice, and gradually treated with a small quantity of alcoholic potassium hydroxide. The mixture soon turns deep brown and deposits a black solid; after being kept for a day at the ordinary temperature, the reaction is complete. The solid is collected, washed with cold alcohol, and dissolved in boiling methylated spirit (about 2·5 litres are required); on cooling, beautiful green prisms (9 to 9·5 grams) separate from the bluish-black solution, which, after a second crystallisation from the same solvent, melt and decompose at 174°:

0·1862 gave 0·4960 CO_2 and 0·1020 H_2O. C = 72·65; H = 6·08.
0·1948 ,, 0·5194 CO_2 ,, 0·1045 H_2O. C = 72·73; H = 5·96.
0·1890 ,, 21·8 c.c. N_2 at 18° and 761 mm. N = 13·33.
0·1895 ,, 22·2 c.c. N_2 ,, 21° ,, 765 mm. N = 13·41.
$C_{25}H_{26}O_2N_4$ requires C = 72·46; H = 6·28; N = 13·56 per cent.

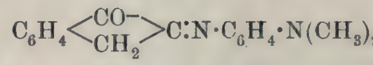
It will be noticed that the agreement between the analytical and theoretical numbers is not so close as might be desired, and that, especially, the percentage of hydrogen was found lower than required for the formula. On account of this discrepancy, I have frequently analysed this compound after repeated crystallisations, but without arriving at results which differ appreciably from those stated above.

The substance $C_{25}H_{26}O_2N_4$ may be regarded as the *hydrate* of 2:3-*bis*(p-*dimethylaminoanilo*)-α-*hydrindone*,



$$\begin{array}{l} C_6H_4\cdot C{:}N\cdot C_6H_4\cdot N(CH_3)_2 \\ CO—C{:}N\cdot C_6H_4\cdot N(CH_3)_2 \end{array}, H_2O.$$

It is only sparingly soluble in alcohol, moderately so in hot benzene, but does not readily crystallise from this solution without the addition of alcohol; it dissolves with great ease in glacial acetic acid to yield an indigo-blue solution, which, in a short time, changes to yellow, and finally, if warmed, becomes reddish-violet. The dark brown filtrate from the compound $C_{25}H_{26}O_2N_4$, when kept for a few days, deposits a very small quantity of a yellowish-red solid. This is moderately soluble in boiling alcohol to form a red solution, from which, on cooling, dark red crystals separate. These have a bluish-green, metallic lustre, and melt at 238°. As mentioned before, the substance is most probably the p-*dimethylaminoanil* of *a-hydrindone*,



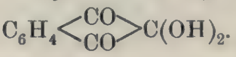
$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO-}{CH_2}{>}C{:}N\cdot C_6H_4\cdot N(CH_3)_2.$$

The following analysis indicates that it is not quite pure:

0·1910 gave 0·5348 CO_2 and 0·1100 H_2O. $C=76·36$; $H=6·39$.

$C_{17}H_{16}ON_2$ requires $C=77·27$; $H=6·06$ per cent.

Triketohydrindene Hydrate,



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C(OH)_2.$$

Dilute sulphuric acid attacks the compound $C_{25}H_{26}O_2N_4$ even at the ordinary temperature, but more readily on slightly warming on the water-bath; the green crystals disappear, and a dark solution is produced. which contains the hydrate of triketohydrindene. Owing to the fact that it is moderately soluble in cold, readily so in boiling, water, but sparingly so in ether, its isolation is rather troublesome. It was found necessary to shake the deep brown liquor which is formed by the action of the acid on the condensation product (10 grams) twenty times with fresh quantities of ether to extract the triketone hydrate (3·2 grams) which was formed. The red, ethereal extracts are decolorised with animal charcoal and evaporated on the water-bath, when a yellow oil is left which solidifies on stirring with a glass rod. The solid readily dissolves in hot water, and, on cooling the concentrated solution, crystallises in colourless prisms, which turn red at 125°, froth at 139°, and melt and decompose at 239—240°. The compound, after drying in a vacuum desiccator over sulphuric acid, gave the following results:

0·2083 gave 0·4637 CO_2 and 0·0640 H_2O. $C=60·71$; $H=3·41$.

$C_9H_6O_4$ requires $C=60·67$; $H=3·37$ per cent.

The aqueous solution of this substance colours the skin purple; this is similar to the behaviour of alloxan, which, in constitution, shows a certain resemblance to triketohydrindene. This substance reduces Fehling's solution as well as ammoniacal silver solutions.

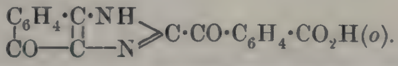
Action of Ammonia on Triketohydrindene.

If the solution of triketohydrindene in dilute ammonia is kept for a short time, it becomes reddish-violet, and no longer reduces silver nitrate. On the addition of dilute hydrochloric acid to the ammoniacal solution, a red, gelatinous precipitate is formed.

This is insoluble in water, sparingly soluble in ether, readily so in hot glacial acetic acid, moderately so in boiling alcohol, and, on cooling the alcoholic solution, crystallises in scarlet prisms. On heating, their colour changes to yellow at about 245°, and above 330° they melt to a dark liquid:

0·1910 gave 0·4760 CO_2 and 0·0540 H_2O. C = 67·96; H = 3·14.
0·2013 ,, 15·6 c.c. N_2 at 20° and 758 mm. N = 8·83.
$C_{18}H_{10}O_4N_2$ requires C = 67·92; H = 3·14; N = 8·80 per cent.

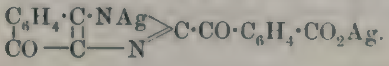
As mentioned above (p. 1442), the compound is most probably to be represented thus:



It dissolves in ammonia, potassium hydroxide, or sodium carbonate to yield reddish-violet solutions, which do not reduce silver nitrate or alkaline copper oxide solutions. The deep violet *silver* compound which it forms on the addition of silver nitrate to its solution in ammonia (containing only a slight excess of the base) is characteristic. If the solution is hot, a curdy, violet precipitate is produced, which is insoluble in water, and can be dried in the water-bath without undergoing any change:

0·2168 gave 0·0880 Ag. Ag = 40·59.
$C_{18}H_8O_4N_2Ag_2$ requires Ag = 40·60 per cent.

In the light of the view expressed above concerning the constitution of the condensation product of the triketone with ammonia, the formula of the silver salt is to be expressed thus:



Action of Aniline on Triketohydrindene.

Aniline reacts with the triketone as readily as does ammonia, and yields a yellow compound which separates in needles on bringing the aqueous solution of the triketone into contact with the base. This substance, however, is very unstable, it darkens at 78°, melts indefinitely at 97°, and, on heating with alcohol, suffers a change which is indicated by a deep violet coloration of the solution. I have not yet further examined this reaction.

Action of Potassium Hydroxide on Triketohydrindene.

If potassium hydroxide (containing about 15 per cent. KOH) is added to the triketone, the crystals turn yellow, and then dissolve to yield a solution which, at first, is yellow, but, on keeping for a short time at the ordinary temperature, becomes colourless. The result is, however, different if one does not wait until the last change occurs, but warms at once after the addition of the alkali to the triketone; under these conditions, a deep blue solution is formed, which retains its colour even on boiling, but becomes colourless on dilution with water, and then does no longer reduce alkaline copper oxide. The interpretation of this remarkable phenomenon I hope to be able to give in my next paper on triketohydrindene.

Diphenylhydrazone of Triketohydrindene, $C_9H_4O(:N\cdot NH\cdot C_6H_5)_2$.

This compound is formed on adding phenylhydrazine to the solution of the triketone in acetic acid; after a short time, a red, crystalline solid separates, which dissolves in a large quantity of boiling alcohol, and, on cooling, crystallises in orange needles, melting at 207—208°:

0·1737 gave 0·4717 CO_2 and 0·0735 H_2O. C = 74·06; H = 4·70.
0·1738 ,, 25·2 c.c. N_2 at 19° and 755 mm. N = 16·56.
$C_{21}H_{16}ON_4$ requires C = 74·12; H = 4·70; N = 16·47 per cent.

The dihydrazone dissolves in cold concentrated sulphuric acid to yield a deep brown solution, which turns indigo-blue on the addition of a trace of potassium dichromate.

Disemicarbazone of Triketohydrindene, $C_9H_4O(:N\cdot NH\cdot CO\cdot NH_2)_2$.

On mixing aqueous solutions of the triketone (1 gram) and semicarbazide hydrochloride (2 grams), an orange coloration is produced, and a yellow solid soon begins to separate. The reaction is complete after keeping the mixture at the ordinary temperature for a day. The substance is sparingly soluble in water or alcohol, and crystallises from these solutions in microscopic, yellow needles, which darken at 175° and melt at 208° with evolution of gas:

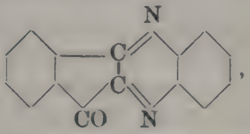
0·1620 gave 43·4 c.c. N_2 at 20° and 758 mm. N = 30·55.
$C_{11}H_{10}O_3N_6$ requires N = 30·66 per cent.

Action of Hydroxylamine on Triketohydrindene.

This reaction takes place if the aqueous solution of the mixture of triketohydrindene hydrate (1 gram) and hydroxylamine hydrochloride (2 grams) is kept at the ordinary temperature; a white solid is gradually formed, and after three days the separation is complete. The solid is sparingly soluble in water or alcohol, but separates very slowly from these solutions in the form of an amorphous powder, which dissolves in potassium hydroxide to yield a red solution, and melts at 174° with rapid evolution of gas. This product is a mixture of oximino-derivatives of triketohydrindene; its chief constituent is the trioxime, $C_9H_4(:NOH)_3$; this is indicated by the following analysis:

0·1875 gave 30·8 c.c. N_2 at 20° and 755 mm. N = 18·66.
$C_9H_7O_3N_3$ requires N = 20·49 per cent.

Ketohydrindenophenazine,



On mixing equal weights of triketohydrindene hydrate and *o*-phenylenediamine, dissolved in hot dilute acetic acid, a yellow solid is precipitated. This is sparingly soluble in cold, moderately so in boiling, alcohol, and, on cooling, crystallises in yellow prisms, which melt at 218—219°. The yield is almost theoretical:

0·1950 gave 0·5550 CO_2 and 0·0635 H_2O. C = 77·62; H = 3·62.
0·1755 „ 18·8 c.c. N_2 at 24° and 767 mm. N = 12·13.
$C_{15}H_8ON_2$ requires C = 77·59; H = 3·45; N = 12·07 per cent.

In conclusion, I may state that I am continuing the research on triketohydrindene as well as the study of the cyclic diketonic compounds which stand in a close relation to isatin.

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CXXXIII.—*The Constitution and Mutarotation of Sugar Anilides.*

By JAMES COLQUHOUN IRVINE and DAVID MCNICOLL, M.A., B.Sc. (Carnegie Scholar).

IN continuation of previous work (Trans., 1908, **93**, 1429; 1909, **95**, 1545) on the rotatory powers and constitution of sugar derivatives containing nitrogen, we have prepared and examined the anilides of tetramethyl mannose, tetramethyl galactose, and trimethyl rhamnose, each of which has been obtained crystalline in forms which exhibit extensive mutarotation. These new compounds may prove useful in the identification of the parent sugars, as, whilst the latter are syrups, the anilides are readily crystallised, and their melting points lie far apart. For comparison, the anilides of the corresponding unsubstituted sugars have been re-examined, and these compounds have also been isolated in mutarotatory forms. As attempts to prepare anilides from tetramethyl fructose and trimethyl arabinose have, so far, resulted in the formation of syrupy products, these compounds are not included in the present paper.

The optical behaviour of the compounds described, and the rotatory changes observed in the course of their formation show that they are comparable with glucoseanilide and tetramethyl glucoseanilide, and it would thus appear that the glucosidic structure suggested for the latter compounds can be generally applied to the anilides of the sugar group. Owing to the ready hydrolysis undergone by such compounds, experimental evidence bearing directly on their constitution is difficult to obtain, but we have been able to apply the silver oxide reaction to the alkylated anilides now described, and find that in each case the compounds resist the methylating effect of the reagent completely. This result is consistent with the idea that the compounds in question are γ-oxides. It should be stated that several cases are now known in which the silver oxide reaction is not effective in alkylating hydroxyl groups, and thus negative results obtained in this way must be applied with caution in determining hydroxyl contents with a view to establishing constitution, particularly where tertiary groups are concerned. From unpublished results obtained in this laboratory, it would appear that ditertiary glycols are either not affected or give only monomethyl ethers (see also McKenzie and Wren, Trans., this vol., p. 476), and another example in which the reagent gives a negative result is quoted by Meldola and Hay (Trans., 1909, **95**, 1379) in the case of a substituted phenol. In the present instance, however, the results obtained by the process are apparently valid, as, in the event of the compounds in question belonging to the aldehydic type, they would contain an unsubstituted secondary alcohol group in the γ-position. Such groups are known to undergo normal alkylation where the requisite solubilities are available, and as we find that mannitol is completely methylated by this reaction, there is thus evidence that all secondary alcohol groups in the sugar residue, irrespective of their position in the carbon chain, may be estimated by this process. The possibility of applying other reagents to anilides is practically excluded, as the compounds are hydrolysed with extreme ease, in some cases even by heating with 90 per cent. alcohol, or with unpurified ether.

The details of the mutarotations are included with the experimental part, and only the principal results are tabulated below, the figures being given to the nearest whole numbers.

Mutarotation of Methylated and Unmethylated Anilides.

	Mannose.	Galactose.	Rhamnose.	Glucose.
$[\alpha]_D^{20°}$ Unsubstituted anilides ...	$-172° \rightarrow -82$ (pyridine)	$-87 \rightarrow -7$ (90% alcohol)	$+137 \rightarrow +77$ (alcohol)	$+10^* \rightarrow -52$ (methyl alcohol)
$[\alpha]_D^{20°}$ Methylated anilides ...	$-98° \rightarrow -39$ (acetone)	$-77 \rightarrow +35$ (acetone)	$+138 \rightarrow +7$ (alcohol)	$+224 \rightarrow +47$ (methyl alcohol)

* Irvine and Gilmour, *loc. cit.*; Gilmour, Proc., 1909, **25**, 225.

Owing to solubility considerations it was necessary to make use of different solvents in determining the mutarotations, and thus accurate comparison of the results is impossible, but it will be seen that the optical changes shown by corresponding pairs of compounds are of the same order throughout, and that the unsubstituted anilides are thus brought into line with the γ-oxidic anilides prepared from the methylated sugars. A qualitative comparison of the optical effect on the parent sugars of glucoside and aniline formation respectively, and also of the influence of methylation on each class of compound, shows certain regularities which are summarised below. The rotatory power of the α-form of the reducing sugar is taken as the basis of comparison, and the signs + and − represent an increase or decrease of specific rotation in the dextro-sense shown by the corresponding methylaldosides and in the maximum initial values of the anilides:

	Mannose.	Galactose.	Rhamnose.	Glucose.
Effect of anilide formation	−	−	+	−
,, methylation on anilide...	+	+	+	+
,, α-methylaldoside formation.........	+	+	−	+
,, methylation on α-methylaldoside .	−	−	−	−

The effect of anilide formation is thus uniformly opposite to that due to α-glucoside formation, and the same holds true for the effect of methylation on each type of compound. The mutarotatory anilides now examined thus closely resemble the β-methylglucosides so far as optical considerations are concerned.

EXPERIMENTAL.

Tetramethyl Mannoseanilide.

A 30 per cent. ethyl-alcoholic solution of tetramethyl mannose (Trans., 1905, **87**, 1462) (1 mol.) was boiled with an excess of aniline (8 mols.) for three hours. After removal of the solvent and excess of the base by evaporation under diminished pressure, a dry, crystalline solid remained, which was recrystallised from petroleum of high boiling point. The *anilide*, which was thus obtained in almost quantitative amount, consisted of slender prisms, melting at 142—143°:

Found, $C=61{\cdot}51$; $H=8{\cdot}19$; $OMe=38{\cdot}59$.

$C_{12}H_{13}ON(OMe)_4$ requires $C=61{\cdot}74$; $H=8{\cdot}04$; $OMe=39{\cdot}87$ per cent.

The compound was readily dissolved in the cold by all ordinary organic solvents with the exception of light petroleum. Although perfectly stable when exposed in air, the compound was very easily hydrolysed. Even boiling with commercial ether was sufficient to decompose it completely into its constituents. It was thus necessary to use specially purified reagents in the preparation and manipulation of the compound.

The optical changes shown by the compound in solution are greatly accelerated by the presence of traces of catalysts, and are not detectable unless special precautions are taken to clean the polarimeter tube and its accessories.

Solvent.	*c.*	Initial $[\alpha]_D^{20°}$.		Final $[\alpha]_D^{20°}$.
Methyl alcohol	2·161	−87·9°	→	−8·3°
Acetone	2·031	−95·5	→	−38·9

In the case of the solution in methyl alcohol, mutarotation proceeded spontaneously, and was generally complete in three to four hours. On the other hand, the acetone solution preserved a constant rotatory power until a trace of acid was added. Apparently a different equilibrium is established in the two solvents, judging from the greater difference shown by the end points as compared with the initial values.

Mannoseanilide.

The following process proved most effective for the rapid preparation of this compound. Fifteen grams of the sugar (1 mol.) were dissolved in boiling methyl alcohol, and 45 grams of aniline (6 mols.) were then added. The separation of the crystalline product commenced almost immediately, and after boiling for half an hour the reaction was complete. The yield was practically quantitative, and the compound separated in the pure state, as repeated crystallisation from boiling water had no effect on the melting point or specific rotation:

Found, C=56·30; H=6·98; N=5·41.

$C_{12}H_{17}O_5N$ requires C=56·47; H=6·67; N=5·49 per cent.

Mannoseanilide crystallises in rectangular prisms, melting with complete decomposition at 181°. The compound is insoluble in all ordinary solvents, with the exception of pyridine and boiling water. The mutarotation observed in pyridine solution ($c=2$) was $[\alpha]_D^{20^\circ}$ $-178·5° \longrightarrow -81·5°$.

In order to obtain, if possible, a specimen of the compound showing mutarotation in the opposite direction, the anilide was also prepared by the method of slow condensation in the cold. A 5 per cent. solution of mannose in 85 per cent. alcohol was prepared at the boiling point of the solvent, and kept for eight hours until the rotation at 20° was constant. Aniline (8 mols.) was then added, and polarimetric readings of the solution were taken, at first every few minutes and afterwards at intervals of fifteen minutes. The curve representing the optical changes showed a perfectly regular change from dextro- to lævo-rotation. Some of the results are appended:

Time, in minutes, from first reading	0	10	70	120	215
Specific rotation	+23·7°	+18·0°	+0·0°	−12·3°	−31·4°

No further readings beyond the last mentioned were possible, as a quantity of the product suddenly crystallised in the polarimeter tube. The filtrate was now *dextro*-rotatory, and the specific rotation, calculating *c* by subtracting the weight of sugar contained in the separated anilide from that originally present in solution, was now +24·0°, a value equal to that observed at the beginning of the condensation. The same held true for the removal of subsequent crops of the product, the specific rotation of the mother liquor, calculated as above, always showing a return to the initial value, indicating that uncondensed sugar in the equilibrium condition was the only active constituent in the filtrate. This behaviour brings the condensation into line with the formation of the alkylmannosides, where, similarly, only one stereoisomeride is produced. All the crops of the anilide had the same melting point (181°), and showed the same mutarotation in pyridine solution:

	Initial $[\alpha]_D^{20^\circ}$.		Final $[\alpha]_D^{20^\circ}$.
First crop	−171·8°	⟶	−82·0°
Final ,, ...	171·0	⟶	81·2

There is thus evidence for the production of only one form of mannoseanilide irrespective of whether the condensation is conducted slowly in ethyl alcohol or at the boiling point of methyl alcohol, and although mutarotation indicates the existence of a second form, all attempts failed to isolate this isomeride or a mixture of the two forms showing downward mutarotation in the dextro-sense. A solution in pyridine, which had attained the constant specific rotation $-81·5°$ when evaporated to dryness under diminished pressure, yielded the equilibrium mixture $[\alpha]_D^{20°}$ $-81·0°$ in the crystalline state. When heated with solvents, this was rapidly converted into the mutarotatory lævo-form.

Tetramethyl Galactoseanilide.

This compound, prepared from tetramethyl galactose (Irvine and Cameron, Trans., 1904, **85**, 1071), is sparingly soluble in ethyl alcohol, from which it separates in rectangular prisms, melting at 192°. The yield is quantitative:

Found, C = 61·60; H = 8·30; OMe = 38·65.

$C_{12}H_{13}ON(OMe)_4$ requires C = 61·74; H = 8·04; OMe = 39·87 per cent.

The compound resembled the other alkylated anilides examined, with the exception that it is much more sparingly soluble in the usual solvents. The optical rotations were accordingly observed in acetone solution at 30°. The mutarotation then observed in a 1 per cent. solution was $[\alpha]_D^{30°}$ $-77·1° \longrightarrow +37·7°$.

Galactoseanilide.

Sorokin (*J. Russ. Phys. Chem. Soc.*, 1886, **18**, 129) describes the preparation of this compound, and states that it melts at 147°. Various specific rotations for the substance are quoted, the value $-33·1°$ being given for methyl alcohol, and $-31·3°$ for a solution in 90 per cent. ethyl alcohol. These values are now corrected.

A 6 per cent. solution of galactose (1 mol.) in 90 per cent. ethyl alcohol, containing excess of aniline (5 mols.), was prepared at the boiling point of the solvent. When the sugar had completely dissolved, the solution was concentrated to half volume and precipitated with dry ether. Galactoseanilide was thus obtained in good yield, and, after recrystallisation from dilute alcohol, the compound melted with slight decomposition at 151°. Mutarotation was only detected with difficulty, as the compound is sparingly soluble, and in the preparation of the solutions for observation of the rotatory power, gentle warming of the solvent is necessary so that readings may be taken without delay:

Solvent.	c.	Initial $[\alpha]_D^{20°}$.		Final $[\alpha]_D^{20°}$.
90 per cent. ethyl alcohol ...	2·325	−86·9°	⟶	−6·88°
90 ,, ,, ,, ...	2·294	88·5	⟶	6·97
Methyl alcohol	0·507	76·9	⟶	31·60

The low concentration used in the case of the methyl-alcoholic solution is explained by the fact that in this case solution was effected in the cold. With $c = 1{\cdot}687$, the solvent had to be warmed before solution was complete, and practically no mutarotation was detected. It is thus evident that the specific rotations previously found for this substance are reliable only so far as the permanent value in methyl alcohol is concerned. On the other hand, the rotations quoted in the literature for ethyl-alcoholic solutions evidently represent intermediate values observed before mutarotation was complete.

The progress of the condensation of galactose with aniline was followed, as usual, polarimetrically, the customary excess of aniline being added to a 5 per cent. solution of the sugar in 65 per cent. alcohol. The condensation at first proceeded very rapidly, and after six hours the solution was lævorotatory. The rotation became constant after eight days, but as the curve representing the optical changes was perfectly regular, no indication was obtained of the formation of the dextrorotatory form of the anilide.

Trimethyl Rhamnoseanilide.

This compound was readily obtained from trimethyl rhamnose by the method already described for the preparation of tetramethyl mannoseanilide. The product was recrystallised from light petroleum, and was then obtained in needles, melting at 111—113°:

Found, $C = 63{\cdot}90$; $H = 8{\cdot}21$; $OMe = 32{\cdot}5$.

$C_{12}H_{14}ON(OMe)_3$ requires $C = 64{\cdot}01$; $H = 8{\cdot}25$; $OMe = 33{\cdot}1$ per cent.

The compound displayed the usual solubilities of alkylated anilides, was very easily hydrolysed, and showed extensive mutarotation:

Solvent.	*c.*	Initial $[\alpha]_D^{20°}$.		Final $[\alpha]_D^{20°}$.
Ethyl alcohol …………	1·1840	+138·5°	→	+16·9°
Acetone …………………	1·2150	138·3	→	46·9

From the identity of the initial rotations and the divergence shown by the permanent values, it would appear that a different equilibrium is attained in the two solvents.

Rhamnoseanilide.

This compound has already been prepared by Rayman and Kruis (*Bull. Soc. chim.*, 1887, [ii], **48**, 463), who describe it as melting at 118°. No rotation values are quoted, the statement merely being made that the compound is dextrorotatory. A 20 per cent. ethyl-alcoholic solution of anhydrous rhamnose was boiled with aniline (5 mols.) for one and a-half hours, the product being isolated as in the case of mannoseanilide. The anilide was crystallised from a mixture of alcohol and light petroleum, and consisted of rectangular prisms, melting at 144°:

Found, C = 60·15; H = 7·32; N = 5·74.

$C_{12}H_{17}O_4N$ requires C = 60·25; H = 7·32; N = 5·85 per cent.

The observed mutarotation in absolute alcohol was $[\alpha]_D^{20°} + 95·8° \longrightarrow 76·0°$. Recrystallisation from ethyl acetate effected a better separation of the mutarotatory forms, the maximum rotation changes then observed being $[\alpha]_D^{20°} + 136·9° \longrightarrow 77·1°$. Experiments conducted with the object of separating the form showing the converse change gave negative results.

Polarimetric Examination of the Condensation.—All the materials used were anhydrous, and precautions were taken to prevent the access of moisture during the process. This was necessary to prevent the optical changes being complicated by the addition of water to the anhydrous sugar. An 8 per cent. solution of dry rhamnose in absolute ethyl alcohol containing 24 per cent. of aniline was prepared at 20° and kept in the dark. The initial specific rotation, calculated on the weight of sugar present, was −5·4°. In one hour the solution was dextrorotatory, and in forty-eight hours the process was complete. The curve representing the optical changes was regular, and this was also the case when the reaction was carried out at 50° with a more concentrated solution of the sugar (20 per cent.). In each case, however, the curve indicated that the form showing upward mutarotation in the dextro-sense was the first to be produced.

We take this opportunity of expressing our indebtedness to the Carnegie Trust for a research grant in aid of the investigation.

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CXXXIV.—*Condensations of Phenanthraquinone with Ethyl Malonate and Ethyl Acetoacetate.*

By MARION BROCK RICHARDS (Carnegie Scholar in the University of Aberdeen).

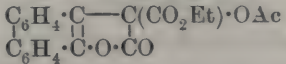
JAPP AND WOOD (Trans., 1905, **87**, 712) described some condensations of phenanthraquinone with ketonic compounds under the influence of acetic anhydride containing a little concentrated sulphuric acid.

The condensation products of phenanthraquinone with ethyl malonate and with ethyl acetoacetate, of which mention was made in that paper, have now been further investigated.

Condensation of Phenanthraquinone with Ethyl Malonate.

Fifty grams of finely powdered phenanthraquinone (free from anthraquinone *), 100 grams of ethyl malonate, 200 grams of acetic anhydride, and 30 grams of concentrated sulphuric acid were heated to 50° for seven days.† The crystals which had separated, and the mother liquor, each yielded a condensation product.

Ethyl 2-Keto-3-acetoxy-4 : 5-diphenylene-2 : 3-dihydrofuran-3-carboxylate,



$$\begin{matrix} C_6H_4\cdot C\text{—}C(CO_2Et)\cdot OAc \\ C_6H_4\cdot C\cdot O\cdot CO \end{matrix}$$

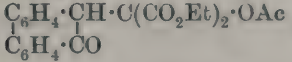
(m. p. 163·5°).

The foregoing crystals, after recrystallisation from alcohol, yielded white, glistening scales, melting at 163·5°. From benzene, on the addition of light petroleum, the substance crystallised in clusters of flat needles. The yield was 29 grams:

0·2036 gave 0·5148 CO_2 and 0·0800 H_2O. $C = 68·96$; $H = 4·37$.

$C_{21}H_{16}O_6$ requires $C = 69·23$; $H = 4·40$ per cent.

Ethyl Phenanthroxylacetoxymalonate,



$$\begin{matrix} C_6H_4\cdot CH\cdot C(CO_2Et)_2\cdot OAc \\ C_6H_4\cdot CO \end{matrix}$$

(m. p. 109·5°).

The acetic anhydride mother liquor, after treatment with water and alcohol, yielded a substance which crystallised from ether in large, white, lustrous prisms, and from alcohol partly in prisms and partly in fine needles, each form melting at 109·5°:

0·2013 gave 0·4963 CO_2 and 0·0973 H_2O. $C = 67·24$; $H = 5·37$.

$C_{23}H_{22}O_7$ requires $C = 67·32$; $H = 5·37$ per cent.

When this substance was treated at 50° with the mixture of acetic anhydride and sulphuric acid, white crystals separated, which after recrystallisation from alcohol melted at 163·5°, and were identified by a mixed melting-point test as the foregoing compound, $C_{21}H_{16}O_6$, showing that the present compound is an intermediate stage in the formation of the previous one.

The formation of these compounds may be explained on the assumption that the unknown ethyl phenanthroxylenemalonate (I) is first formed; this compound then unites with acetic acid, and the additive compound (II) loses alcohol:

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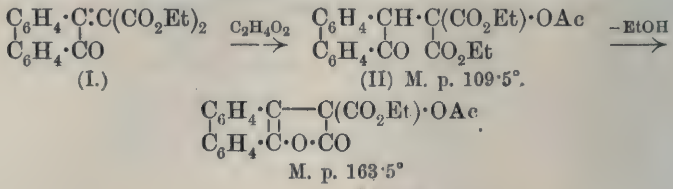
* The phenanthraquinone used for these reactions must be purified by means of the sodium hydrogen sulphite compound, as some of the products are almost impossible to separate from the anthraquinone which will otherwise contaminate them.

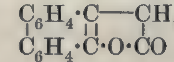
† If the usual proportion of sulphuric acid is employed, namely, 3 grams of acid to 100 grams of acetic anhydride, the condensation takes much longer.



$$\begin{array}{l} C_6H_4\cdot C{:}C(CO_2Et)_2 \\ C_6H_4\cdot CO \end{array} \xrightarrow{C_2H_4O_2} \begin{array}{l} C_6H_4\cdot CH\cdot C(CO_2Et)\cdot OAc \\ C_6H_4\cdot CO\ \ CO_2Et \end{array} \xrightarrow{-EtOH} \begin{array}{l} C_6H_4\cdot C{-}C(CO_2Et)\cdot OAc \\ C_6H_4\cdot C\cdot O\cdot CO \end{array}$$

(I.) (II) M. p. 109·5°. M. p. 163·5°

2-*Keto*-4 : 5-*diphenylene*-2 : 3-*dihydrofuran*,

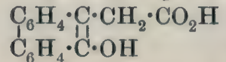


$$\begin{array}{l} C_6H_4\cdot C{-}CH_2 \\ C_6H_4\cdot C\cdot O\cdot CO \end{array}$$ (m. p. 177°).

Fifteen grams of the substance $C_{21}H_{16}O_6$ (m. p. 163·5°), 12 grams of red phosphorus, and 100 grams of hydriodic acid (D 1·7) were boiled together for four hours under reflux. The solid substance was extracted first with ether, and, on evaporating off the ether, a small quantity of substance was obtained which crystallised from benzene in needles. The residue was then extracted with boiling benzene, and from this extract there separated clusters of long, silky, colourless needles, melting at 177°. The yield was about 8½ grams:

0·1476 gave 0·4447 CO_2 and 0·0575 H_2O. C = 82·17; H = 4·33.
$C_{16}H_{10}O_2$ requires C = 82·05; H = 4·27 per cent.

9-*Hydroxy*-10-*phenanthrylacetic Acid*,



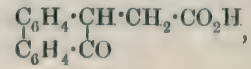
$$\begin{array}{l} C_6H_4\cdot C\cdot CH_2\cdot CO_2H \\ C_6H_4\cdot C\cdot OH \end{array}$$ (m. p. 182—183°).

The lactone was dissolved in aqueous potassium hydroxide on the water-bath, the solution acidified with hydrochloric acid, and the precipitated acid collected and dried at 100°. The yield was quantitative. The acid was difficult to purify by recrystallisation, as the solutions very readily oxidised, turning green or orange-coloured. For analysis it was crystallised from a mixture of acetone and benzene, from which it was obtained in colourless prisms. It melted, when rapidly heated, at 182—183°:

0·1839 gave 0·5123 CO_2 and 0·0801 H_2O. C = 75·98; H = 4·84.
$C_{16}H_{12}O_3$ requires C = 76·19; H = 4·76 per cent.

Boiling with acetic anhydride reconverted the acid into the lactone.

In view of the possible formulation of the acid as



$$\begin{array}{l} C_6H_4\cdot CH\cdot CH_2\cdot CO_2H \\ C_6H_4\cdot CO \end{array},$$

the action of hydroxylamine was tried, but no oxime was obtained.

That the acid contains a phenolic hydroxyl group is shown by the fact that the monopotassium salt, which is sparingly soluble in water, readily dissolves in excess of potassium hydroxide, doubtless yielding the dipotassium salt. From this solution carbon dioxide reprecipitates the monopotassium salt.

The salts of the acid, like the acid itself, decomposed very readily. The silver salt turned dark soon after it was precipitated, whilst the sodium and barium salts decomposed when attempts were made to recrystallise them, and had therefore to be analysed direct.

Barium Salt.—This salt was prepared by precipitating the ammonium salt with barium chloride. It was dried in the air:

0·3958 lost, at 110°, 0·0406 H_2O. $H_2O = 10{\cdot}26$.

$(C_{16}H_{11}O_3)_2Ba,4H_2O$ requires $H_2O = 10{\cdot}13$ per cent.

0·3552 anhydrous salt gave 0·1324 $BaSO_4$. $Ba = 21{\cdot}93$.

$(C_{16}H_{11}O_3)_2Ba$ requires $Ba = 21{\cdot}48$ per cent.

Sodium Salt.—This salt was prepared by boiling the acid with a solution of sodium carbonate. It crystallised in fine needles, which were dried at 110°:

0·3905 anhydrous salt gave 0·0995 Na_2SO_4. $Na = 8{\cdot}25$.

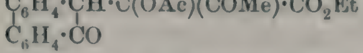
$C_{16}H_{11}O_3Na$ requires $Na = 8{\cdot}39$ per cent.

Condensation of Phenanthraquinone with Ethyl Acetoacetate.

The condensation of phenanthraquinone with ethyl acetoacetate in the presence of dilute aqueous potassium hydroxide has already been studied by Japp and Streatfeild (Trans., 1883, **43**, 28) and Japp and Klingemann (Trans., 1891, **59**, 1); but the results differ entirely from those obtained by the method here described.

Fifty grams of finely powdered phenanthraquinone, 80 grams of ethyl acetoacetate, 200 grams of acetic anhydride, and 6 grams of concentrated sulphuric acid were kept at about 20° for about a fortnight. The mixture was then filtered, 15 grams of a brown solid being obtained. At the slightly higher temperature of 30°, the yield is reduced to 5 grams.

Ethyl 9-Phenanthroxylacetoxyacetoacetate,



$$\begin{array}{l} C_6H_4\cdot CH\cdot C(OAc)(COMe)\cdot CO_2Et \\ C_6H_4\cdot CO \end{array}$$

(m. p. 148°).

The brown solid was boiled with benzene, and the solution filtered from a small quantity of yellow, insoluble substance. The benzene solution deposited colourless prisms, which melted finally at 148°. These turned yellow on exposure to light:

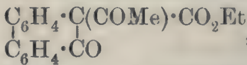
0·1991 gave 0·5070 CO_2 and 0·0946 H_2O. C = 69·45; H = 5·28.
$C_{22}H_{20}O_6$ requires C = 69·47; H = 5·26 per cent.

Compound, $C_{22}H_{18}O_5$.—The sparingly soluble yellow substance was dissolved in solvent naphtha (b. p. 164—170°), giving a yellow, fluorescent solution, from which there crystallised minute, yellow needles, which did not melt below 315°. On analysis it gave figures pointing to the formula $C_{22}H_{18}O_5$, but the combustion was not conclusive, as the substance left 13 per cent. of ash. Owing to the difficulty in obtaining the substance, no further preparation was made:

0·1313 gave 0·3494 CO_2 and 0·0550 H_2O. C = 72·57; H = 4·65.
$C_{22}H_{18}O_5$ requires C = 72·93; H = 4·97 per cent.

Ethyl phenanthroxylacetoxyacetoacetate, when allowed to remain in the cold with the mixture of acetic anhydride and sulphuric acid, yielded the foregoing dehydration product, $C_{22}H_{18}O_5$; hence the substance melting at 148° is an intermediate stage.

The action of the mixture of acetic anhydride and sulphuric acid at the ordinary temperature on Japp and Streatfeild's ethyl phenanthroxyleneacetoacetate,



$\begin{array}{l}C_6H_4\cdot C(COMe)\cdot CO_2Et\\ C_6H_4\cdot CO\end{array}$

, was also tried, but this yielded only the compounds $C_{20}H_{14}O_3$ (m. p. 285°) and $C_{22}H_{18}O_5$ (m. p. 165—171°), which Japp and Klingemann obtained by the action of acetic anhydride alone on this substance at 150° (Trans., 1891, **59**, 15).

This research was carried out under Professor Japp's supervision, and the author wishes to thank him for the interest he has always taken in the work.

CHEMICAL DEPARTMENT,
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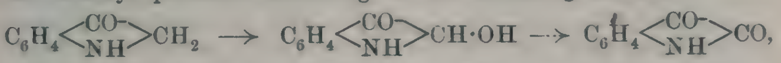
CXXXV.—*Indirubin. Part I.*

By WILLIAM POPPLEWELL BLOXAM and A. G. PERKIN.

IT is well known that certain varieties of natural indigo contain a considerable quantity of indirubin, and it is probable (Trans., 1907, **91**, 279) that at least a trace occurs in all samples of the natural dyestuff. That the indirubin originates from the indican existing in the leaves of the various species of the *Indigofera* which are employed in the manufacturing process, and is due to no second constituent of the plant is now certain, and its production is to be explained in all cases as due to the condensation of isatin with indoxyl according to Baeyer's equation (*Ber.*, 1881, **14**, 1745). Thus, it has been clearly shown (Trans., 1909, **95**, 830) that indigo containing indirubin can be readily produced from crystalline indican by a replica of the factory method, and again an important point in this respect has been the isolation of isatin itself from natural indigo rich in indirubin (Proc., 1907, **23**, 30). The formation of the necessary isatin is favoured by special circumstances, such as oxidation of the indoxyl by air in the presence of alkali or acid, and may also be affected to some extent by temperature. Again, the fact that indoxylic acid (Trans., 1909, **95**, 847) by air-oxidation is readily converted, at least in part, into isatin has been previously discussed, and may have some bearing upon the production of indirubin during the manufacturing process. It is most probable that this so-called "secondary" oxidation of the indoxyl proceeds according to the following scheme:



$$C_6H_4<\begin{matrix}CO\\NH\end{matrix}>CH_2 \longrightarrow C_6H_4<\begin{matrix}CO\\NH\end{matrix}>CH{\cdot}OH \longrightarrow C_6H_4<\begin{matrix}CO\\NH\end{matrix}>CO,$$

and that it is also indirectly the cause of the production of indigo-brown (*loc. cit.*).

With a desire of studying in a quantitative manner the various conditions which are responsible for the formation of indirubin during the manufacture of natural indigo, samples of this dyestuff, which had been prepared in the laboratory from pure indican, were submitted to analysis by methods which are described as suitable for this purpose. The results were, however, not sufficiently accurate either in the case of these laboratory products or with specially prepared mixtures of the pure colouring matters, and it was thus necessary, before proceeding further with the main object of the inquiry, to devise, if possible, a method better suited to our requirements.

It is well known that indirubin is much more resistant to oxidation and reduction than indigotin, properties which also apply to the sulphonic acids of these colouring matters. When dealing therefore with the latter substances under usual analytical conditions, and employing either potassum permanganate * or titanium chloride,* the indigotin is to some extent preferentially attacked, so that towards the end of the operation the colouring matter consists entirely of indirubinsulphonic acid. In the case, however,

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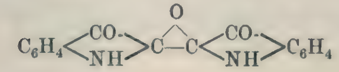
* Experiments have indicated the correctness of Koppeschaar's statement; thus, when 20 c.c. of a solution of indigotinsulphonic acid (1 gram per litre) was treated with potassium permanganate (1 gram per litre) under the conditions of concentration previously given by one of us (*J. Soc. Chem. Ind.*, 1906, **25**, 735), 9 c.c. of the reagent were necessary for its decolorisation, but, on the other hand, for 20 c.c. of indirubinsulphonic acid of the same strength but 7·28 c.c. were required, although the oxidation in the latter case was of a slower character. Curiously enough, with

a mixture of equal parts of the two sulphonic acids, 25 c.c. in all, the total consumption of permanganate was greater than that required for the sum of the two constituents (Found, 10·65 c.c. Theory requires 10·17). Again the amount of reagent employed up to the disappearance of the blue coloration was 6·2 c.c. (theory requires 5·12 c.c.), so that these figures indicate that the original solution contained 60·5 per cent. of indigotin, 45·15 per cent. of indirubin, a total of 105·65 per cent., instead of the amounts above stated. It is evident, therefore, that the permanganate does not discriminate quantitatively between the blue and red sulphonic acids, and could not, therefore, be employed for this purpose, or for the estimation of the total quantity of mixed colouring matters present. The cause of the latter discrepancy originates from the slow oxidation of the indirubinsulphonic acid by the permanganate, which admits of the simultaneous further degradation of the decomposition products of the indigotin which have been produced at the earlier stage of the process.

The action of potassium permanganate on solutions of the indigotinsulphonic acids is of interest, because the amount of the reagent necessary for the decolorisation of the liquid varies, to some extent, with its concentration, and this point has been alluded to by Rawson (*A Dictionary of Dyes, Mordants, etc.*, by Rawson, Gardner, and Laycock, 1901, 187). It has been found, for instance, at the concentration employed by one of us, and which is identical with that recommended by Badische Anilin- und Soda-Fabrik (*Chemistry of Pure Indigo*, B.A.S.F. *brochure*, 1900), that, under these conditions, 1 gram of indigotin as sulphonic acid requires 0·45 gram of permanganate for decolorisation, whereas the equation:

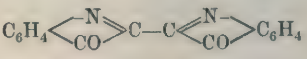
$$5C_{16}H_{10}O_2N_2 + 4KMnO_4 + 6H_2SO_4 = 10C_8H_5O_2N + 2K_2SO_4 + 4MnSO_4 + 6H_2O$$

implies that 0·4824 gram of the reagent is necessary. It is evident, therefore, that this oxidation is of a complex nature, and either consists of two distinct stages in the formation of isatinsulphonic acid or of two distinct reactions involving the production of the two separate substances. As regards the first suggestion, it is possible that the isatin formation would be preceded by that of an intermediate compound (I), or that by the latter in addition to isatin, a dehydroindigotinsulphonic acid (II) is formed.



$$C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C\overset{O}{—}C\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C_6H_4$$

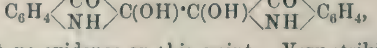
(I.)



$$C_6H_4\left\langle\begin{matrix}N\\CO\end{matrix}\right\rangle C—C\left\langle\begin{matrix}N\\CO\end{matrix}\right\rangle C_6H_4$$

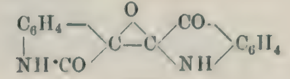
(II.)

In case the first product of the reaction consists entirely of dehydroindigotin, this must prior to further oxidation to isatin take up two molecules of water with formation of dihydroxyindigotin,

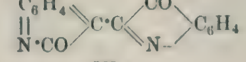


$$C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C(OH){\cdot}C(OH)\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C_6H_4,$$

but there is at present no evidence on this point. Very striking in this respect is the small amount of permanganate required for the decolorisation of indirubinsulphonic acids, and a similar explanation is here available. Either, therefore, the compound (III) or the unknown dehydroindirubin (IV) is produced in the form



(III.)



(IV.)

of the former reagent, it has been stated by Koppeschaar (*Zeitsch. anal. Chem.*, 1899, **38**, 1) that it is not possible to obtain trustworthy figures with indigos in which some quantity of indirubin is present, and Rawson (*J. Soc. Chem. Ind.*, 1899, **18**, 252), although not so emphatic on this point, considers that it is not easy in this manner to obtain accurate results. On the other hand, it is usual to separate the more soluble indirubin from the indigo by a process of extraction, and for this purpose ether (Rawson, *loc. cit.*), acetone (Gardner and Denton, *J. Soc. Dyers*), and acetic acid (Koppeschaar, *loc. cit.*) have been recommended. Rawson's statement that indirubin is easily soluble in ether can only apply to the crude commercial solvent, for it was ascertained by experiment that the pure liquid dissolves but a trace of this colouring matter. In a criticism of Rawson's process, Gardner and Denton (*loc. cit.*) state that the amount of indirubin estimated depends greatly on the length of time the extraction proceeds, and that even after three hours' boiling the indirubin is not completely extracted from the indigo. Experiments with this method fully corroborated the objections raised by the latter authors, and, moreover, the ethereal extract of the colouring matter prepared according to Rawson's directions was of a purple-blue colour, and was not easily comparable with the standard solution of indirubin in ether. Curiously enough, pure acetone was found also to exert but little solvent action towards indirubin, and thus it appears evident that the active agent in both the so-called ether and acetone methods consists in reality of the alcoholic impurity which is present in the com-

of its sulphonic acid. It is considered probable that the dehydroindigotin and dehydroindirubin formation occurs in these respective instances.

On the other hand, with titanium chloride, and employing the process according to the details previously given by one of us, it was found that this reagent behaves in an identical manner towards both indigotin- and indirubin-sulphonic acids, and that the consumption in each case is identical. Moreover, numerous trials carried out with mixtures of the pure sulphonated colouring matters indicated that the amount of the reagent required was, in all cases, equal to the sum of that theoretically necessary for each constituent. This is clearly indicated by the following results:

	Indigotin-disulphonic acid (c.c.).		Indirubin-disulphonic acid (c.c.).	Present, indigotin + indirubin, gram.	Found, indigotin + indirubin, gram.	Found, per cent.
1	15	+	10	0·0250	0·02497	99·90
2	10	+	15	0·0250	0·02505	100·21
3	20	+	5	0·0250	0·02512	100·50
4	5	+	20	0·0250	0·02494	99·77

It was found, however, that it was not possible by means of this reagent to differentiate in a quantitative manner as to the amount of each of the sulphonated colouring matters which were present in the mixture. Although, during the reaction, the blue colour of the liquid disappears and a red stage is ultimately reached, this only occurs before the final transition to bright yellow.

mercial liquids. Indeed, it is pointed out by Gardner and Denton that the quality of the acetone used is of importance.*

It is probable therefore that the failure of experiments to give satisfactory results by the use of the latter method was occasioned to some extent by the nature of the commercial acetone (Kahlbaum's) which was employed. Thus, the addition of the aqueous salt solution to the acetone extract of the indigo in the manner recommended by these authors for the precipitation of impurities unfortunately also caused the deposition of indirubin itself, and, on the other hand, it was observed that a precipitation of the dissolved indigotin from the acetone in this manner was far from complete. Finally, in regard to both the ether and acetone processes, no account is given by their authors of attempts to standardise their processes with mixtures of the pure colouring matters, and their accuracy does not therefore appear to have been submitted to experimental proof.

That indirubin can be completely extracted by means of boiling acetic acid has already been shown in a previous communication (*loc. cit.*), and on this account Gardner and Denton's statement (*loc. cit.*) that Koppeschaar's process is inconvenient on account of the apparent insolubility of the colouring matter in glacial acetic acid and the impossibility of completely extracting it from indigo is difficult to understand. Experiments with this method gave fairly satisfactory results, for, employing a mixture of 99 parts of pure indigotin and 1 part of indirubin, the actual figures obtained were indigotin 97·36, and indirubin 0·976 per cent. In carrying out the process, however, it was discovered that in addition to indirubin the acetic acid also removes a small quantity of indigotin from the indigo, and for trustworthy figures a standard acetic acid solution of the latter colouring matter in addition to that of indigo-red is necessary. Considerable discomfort is, however, occasioned by the employment of the glacial acetic acid in open vessels, although it is probable that with certain modifications this and other minor objections to the method could be overcome.

It has been previously pointed out (Trans., 1907, **91**, 279) that pyridine is an excellent solvent for indirubin and also for indigo-brown, whereas in regard to indigotin its power in this respect is very limited, and it thus appeared possible that an analytical method based on the employment of this liquid could be devised. A necessary feature of such a process was obviously to avoid the use of open vessels, and after repeated trials this was ultimately effected by the process described in the following pages.

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* In this paper, the statement occurs that indigo-brown is soluble in acetone. As the main constituent of indigo-brown (Trans., 1907, **91**, 279) is practically insoluble in all solvents with the exception of pyridine, this can only refer to the trace of the more soluble compound which is present in this mixture.

The qualitative examination of indigo for indirubin is readily effected by digesting the finely-divided dyestuff for a few seconds with a small amount of boiling pyridine. Employing, for instance, a mixture of pure indigotin, 99 per cent., and pure indirubin, 1 per cent., a deep red extract was obtained in this manner, containing but a trace of blue, whereas with indigotin, 99·999 per cent., and indirubin, 0·001 per cent., the supernatant liquid was of a purple-red colour. In the case of natural indigos, the colour of the indirubin, if present in the pyridine extract in but limited amount, may be masked to some extent by the presence of indigo-brown. To remove the latter, the pyridine solution is poured into a small quantity of methylated ether, and the mixture agitated with dilute sodium hydroxide solution. The ethereal layer will then possess the red colour which is characteristic of indigo-red.

The following table indicates the selective action of various solvents at the boiling point on indirubin and indigotin respectively alone, and also on mixtures of these colouring matters in definite proportion:

Solvent.	Indirubin.	Indigotin.	Indigotin, 99 per cent., indirubin, 1 per cent.	Indigotin, 99·999 per cent., indirubin, 0·001 per cent.
Pyridine	Deep currant-red	Intense blue	Deep currant-red	Purple-red
Acetic acid	Deep purple-red	Faint blue	Strong purple	Faint blue only
Acetone............	Red, but less intense	Insoluble	Magenta, but less intense	Faint blue
Methylated ether	Faint reddish-yellow	Insoluble	Magenta, but again less intense	No trace of red

The Pyridine Method.

The finely sieved sample of the air-dried indigo (0·25 to 1 gram) is weighed out into a small beaker, and evenly incorporated with 20 to 30 grams of purified sand. A thin-walled glass tube, approximately 25 × 90 mm., and which, for the sake of convenience, will be referred to as the "container," is neatly closed at one end by means of cotton cloth, which is fastened to the tube with fine string or silk cord (copper or brass wire must not be employed),* and into this is introduced a layer of asbestos covered with sand, or sand alone. With the aid of a Gattermann funnel, the contents of the beaker are now poured in, and the beaker is cleansed from adhering dyestuff by successive washings with sand, which are then added to the main bulk. Sufficient sand is then added to form a layer on the upper surface of the indigo mixture, and the whole is then loosely covered with asbestos, which can be previously employed if necessary to remove the last traces of indigo from the beaker. The container is now placed in a Soxhlet tube, in which it should be fitted somewhat loosely, and in which, in order to promote efficient drainage, two or three glass marbles have already been introduced. Extraction with pyridine is then commenced, the heat being so regulated that a brisk ebullition of the solvent takes place. The first extracts are coloured red, but usually, after the operation has proceeded for about half an hour, the liquid possesses merely the blue colour of pure indigotin. The digestion is then discontinued, and the Soxhlet tube holding the container drained as thoroughly as possible. The contents of the flask, which is preferably of the Erlenmeyer variety, are distilled down to a small bulk. The residual liquid is treated cautiously with boiling water (A), and again distilled, and this operation is repeated until the last traces of the pyridine have disappeared.*

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* In the earlier experiments, the cotton cloth was replaced with copper and brass gauze, and in these analyses a small, but persistent, loss of approximately 2 per cent. of indigotin occurred. This was eventually accounted for by the fact that the pyridine (chemical pure pyridine does not exert a deleterious effect) employed, and apparently all commercial varieties of this liquid, contain a little ammonia, and

On cooling, the precipitate, which consists of a mixture of indirubin and indigotin in a crystalline condition, together with indigo-brown, is collected by means of asbestos in a Gooch crucible and washed with water. As a trace of the indigo-brown is present in combination with calcium or magnesium, and in this condition is insoluble in alkaline liquids, the mixed substances are first washed with hot 15 per cent. hydrochloric acid to remove this mineral matter, and then with hot 1 per cent. sodium hydroxide solution, which now completely dissolves the brown impurity. The product is finally treated with 1 per cent. acetic acid. The crucible and its contents are now placed in a small beaker, and, after drying, 5 c.c. of pure sulphuric acid are added. On heating the mixture for half an hour in a water-oven, sulphonation occurs, and the product is

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that the latter, under the conditions of experiment, caused the formation of cupric hydrate. For instance, if a saturated pyridine solution of indigotin is digested at the boiling point with a little cupric hydrate, the colour of the solution is almost immediately discharged, and this effect was also observed to occur towards the end of the actual analytical process. It is probable that the oxidation product of the indigo which is thus formed is dehydroindigotin (*loc. cit.*).

* The quantity of pyridine employed for the extraction is immaterial, and such diverse quantities as 400 c.c. and 75 c.c. have been found equally useful. The loss of solvent during each analysis has been approximately 15 c.c., and this could, no doubt, be further reduced. König's "pyridin puriss" is excellent for this purpose.

then dissolved in hot water, the liquid filtered into a 250 c.c. flask, and finally diluted to this volume. The quantity of each colouring matter present in this solution as sulphonic acid is estimated by means of the Duboscq colorimeter, by comparison with standard mixtures of pure indigotin- and indirubin-sulphonic acids prepared in a similar manner and containing 1 gram of the colouring matter per litre. As a general rule, the most satisfactory dilution for this purpose was found to be 5 c.c. of the standards, and also of the sample solution in 200 c.c. of water, but in the case of the isolation of mere traces of indirubin a concentration of not less than 5 c.c. of the sample solution in 50 c.c. of water was then necessary.

In order to gauge the accuracy of the colorimetric determinations, the sample solution was also estimated as regards the total amount of colouring matter present by means of titanium chloride. For this purpose 25 c.c. of the solution were employed, together with 10 c.c. of 20 per cent. sodium tartrate, the somewhat excessive quantity of this latter being necessary on account of the large proportion of mineral acid present. In other respects the operation was carried out according to the modification of Knecht's process (*J. Soc. Dyers*, 1903, **3**, 66) employed by one of us in previous work (Bloxam, *J. Soc. Chem. Ind.*, 1906, **25**, 735), except that the titration was performed in purified hydrogen in the place of carbon dioxide.

As will be observed in the subsequent tables, the colorimetric and titanium chloride figures agree closely with one another, and having thus established the accuracy of the former method it will not be necessary in the subsequent use of the process to employ the latter as an adjunct.

The Residual Indigotin.—The container, and its contents which had been extracted by the pyridine without removal from the Soxhlet apparatus, were washed by percolation with water, and in the event of these washings being coloured by means of the trace of the pyridine solution of indigotin which remained in the container, this water was employed at the stage (A) (p. 1466) of the process. Subsequently the residue was repeatedly percolated with boiling 10 per cent. sulphuric acid, which effects the removal of the indigo gluten together with some of the mineral matter, and finally with boiling water until free from acid.

The cloth is now removed from the container, and by gently pushing the upper asbestos layer with a stout glass rod the contents of the tube are transferred to a spouted beaker of about 100 c.c. capacity, an operation which is readily performed without an adherence of any colouring matter to the sides of the tube. The whole is now dried in the water-oven, and after an addition of

20 c.c. of pure sulphuric acid, the colouring matter present is sulphonated in the usual way.

The product diluted with water is filtered into a litre flask, finally made up with water to that volume, and an aliquot portion titrated with potassium permanganate, according to the directions previously given (Bloxam, *loc. cit.*), and in which 1 c.c. of the reagent is equivalent to 0·00222 gram of indigotin.

In order to test the accuracy of the process, known mixtures of the pure colouring matters were at first employed, and the following table illustrates the results obtained:

Composition of mixture.	Total colouring matter, blue by $KMnO_4$, red by $TiCl_3$.	Total colouring matter, by $KMnO_4$ and colorimeter.	Values blue and red respectively by $KMnO_4$ and $TiCl_3$.	Values blue and red respectively by $KMnO_4$ and colorimeter.
Blue 80·00	100·32	99·79	Blue 79·27	78·75
Red 20·00	—	—	Red 21·04	21·04
Blue 85·00	100·17	100·03	Blue 85·20	85·07
Red 15·00	—	—	Red 14·96	14·96
Blue 90·00	100·98	100·84	Blue 90·66	90·52
Red 10·00	—	—	Red 10·32	10·32
Blue 95·00	100·69	99·51	Blue 95·68	94·50
Red 5·00	—	—	Red 5·01	5·01
Blue 99·00	99·96	99·66	Blue 98·82	98·52
Red 1·00	—	—	Red 1·14	1·14

Having therefore ascertained that the method gave sufficiently accurate results, its application to natural indigos was now studied.

It is well known that Java indigo, as a rule, contains appreciable quantities of indirubin, and some varieties of this product, obtained through the kindness of Prof. van Romburgh, were available for examination. These samples were representative of three distinct processes: (*a*) the new process with hot water, (*b*) the new process with cold water, and (*c*) the old process, in which no chemicals are used. The exact manner in which indigo has been manufactured in Java has remained more or less of a secret, so that an examination of these authentic preparations was not devoid of interest.

During the analyses more than one titration of the sulphonated colouring matter was carried out, and the maximum and minimum results are given in the tables.

Java Indigo.—New Process with Hot Water.

No. of sample.	Total red and blue, maximum.	Total red and blue, minimum.	Total blue, maximum.	Total blue, minimum.	Red.
1	75·20	75·10	67·76	67·67	7·43
1	75·00	74·80	67·99	67·79	7·01
1	75·61	75·53	68·23	68·15	7·38
2	73·60	73·37	64·08	63·86	9·51
3	73·46	72·41	66·22	65·76	7·75
4	68·13	66·96	61·41	60·96	5·91
5	67·13	66·55	60·32	59·74	6·81
6	62·91	62·36	57·90	57·35	5·01

Java Indigo.—New Process with Cold Water.

7	72·88	72·29	69·82	69·23	3·06
7	72·82	—	69·50	—	3·32
8	71·02	70·39	66·98	66·35	4·04
9	58·30	57·76	56·15	55·61	2·15
10	71·90	71·46	69·86	69·42	2·04
11	61·71	61·48	59·21	58·98	2·50
12	62·71	62·21	59·18	58·68	3·53

Java Indigo.—Old Process without Chemicals.

13	75·28	—	73·80	73·03	1·48
13	75·28	—	73·88	72·71	1·40
13	75·27	75·06	73·88	73·67	1·39
? 13	74·96	74·63	73·22	72·89	1·74
14	73·10	72·72	71·93	71·55	1·17
14	73·10	72·73	71·88	71·51	1·22
15	69·54	69·25	68·44	68·15	1·10
15	69·54	69·25	68·80	68·26	0·99

Analysis of Results.

	Average value blue and red.	Average value total blue.	Average value red.
New process, hot water	71·62	64·59	7·07
,, ,, cold ,, ...	66·98	64·03	2·95
Old ,, without chemicals.	73·20	71·90	1·30

Somewhat interesting in connexion with the examination of these Java indigo samples is the statement of Koppeschaar in the paper previously referred to, that van Lookeren Campagne has the credit of finding a method of preparing indigo from the Natal plant (*I. arrecta*) in Java which gives twice or thrice the yield. On the other hand, he further remarks that the whole character of the indigo is changed, the percentage of red being much greater than usual, sometimes exceeding 10 per cent. The process here referred to by Koppeschaar, in the light of the above results, would appear to be identical with "the new process with hot water."

It is well known that hot water processes of indigo manufacture have been much favoured by the Dutch manufacturers, and it is reasonable to connect the excessive quantity of indigo-red, which so frequently occurs in the Java variety, with the question of temperature. The air-oxidation of indoxyl solutions in the presence of an excess of alkali or ammonia tends in a similar direction, but it has been shown (Trans., *loc. cit.*) that in these circumstances a decrease in the yield of colouring matter thus occurs, a point which is not likely to have escaped the observation of the Dutch chemists. It was noted during the laboratory experiments on the formation of indigo from pure indican (*loc. cit.*) that the dyestuff thus produced contained somewhat more indirubin than is usually present in most of the Indian commercial samples previously examined (*loc. cit.*), and the only reasonable method for accounting for this discrepancy is the fact that the temperature of the liquid during air oxidation was maintained steadily at 60°. It is to be remembered that this indirubin formation probably occurs at the earlier stage of the oxidation, because the presence of free indoxyl is necessary in order that the reaction with the isatin may take place. On the other hand, with the Indian factory process, the average temperature of the oxidation will be lower, although by the effect of the steam blowers it will ultimately reach this point. Again, Rawson (*Report on the Cultivation and Manufacture of Indigo*, Mozufferpore, 1904) states that after a hot water fermentation the liquid must at once be submitted to oxidation to avoid a subsequent loss of colouring matter, and it would therefore appear to follow that in such a process the temperature during the latter operation is necessarily higher than that in vogue by the ordinary method. It seems likely therefore that the high percentage of red in the new process with hot water samples of Java indigo arises from the fact that during their manufacture the oxidation of indoxyl in the presence of a trace of alkali or ammonia has been carried out at a higher temperature than usual.

Among the Indian varieties of natural indigo, that produced in the past by the "Coventry Lime and Acid process" has been noted as containing some quantity of indirubin. It is referred to by Koppeschaar, who states that Coventry's method is used in British India, and that the indigo prepared by this method contains much indigo-red, but less indigotin than good samples of Java indigo (*loc. cit.*). A description of the process has been given in a previous paper (*loc. cit.*), and the indigo which is there produced arises from the air-oxidation of indoxyl in the presence of lime-water. An authentic sample of this indigo had been preserved in the Dyeing Department of the Leeds University, and was available for examination by the pyridine method. Four distinct analyses of this product were carried out, and the results are given in the following table:

Coventry Process Indigo.

Total red and blue, maximum.	Total red and blue, minimum.	Total blue, maximum.	Total blue, minimum.	Red.
61·76	61·44	56·53	56·21	5·23
61·76	60·77	56·73	55·74	5·03
61·20	60·97	56·50	56·27	4·70
61·38	61·19	56·40	56·21	4·98

Finally, an analysis is given of two samples of indigo prepared in the laboratory, the first of which is curious on account of the large amount of indirubin which it contains. This product (A) was obtained by the hydrolysis of indican (0·9996 gram) with 2 grams of the enzyme for five hours and a-half at 50—52° in the presence of 3·7 c.c. of *N*/10-sulphuric acid, and the operation was carried out in the absence of air and in the manner described fully in a previous communication (*loc. cit.*). The indoxyl solution was then oxidised with air at 60° after the addition of 18·5 c.c. of *N*/2-ammonia, and apparently the whole operation was conducted in the usual manner. The result, however, is quite abnormal, and is merely referred to as showing the possibility of the formation of very large quantities of indirubin during the oxidation process. The second sample (B) represents the product of the hydrolysis of indican by acid and simultaneous oxidation with air, and in which 0·5 gram of indican in 850 c.c. of water at 60° was treated with 15 c.c. of 33 per cent. hydrochloric acid, and air aspirated through the solution for eight hours.

	Total red and blue, maximum.	Total red and blue, minimum.	Total blue, maximum.	Total blue, minimum.	Red.
A	88·90	88·13	63·07	62·30	25·83
B	93·5	—	—	—	2·54

Estimation of Indigo-Brown

A point of interest in this pyridine process for the analysis of indigo containing indirubin is that it is also possible to estimate approximately at the same time the amount of indigo-brown which is present in the sample. It has been previously shown that this mixture of brown substances can be removed from the dyestuff by means of pyridine (Trans., 1907, **91**, 279), and consequently in this analytical method it is contained, or mostly so, in the crude indirubin precipitate which remains after the removal of the solvent. On the other hand, it was ascertained that the aqueous filtrate (A) from this precipitate contains a small quantity of one of the more soluble brown constituents. In carrying out therefore the estimation, the indirubin precipitate is washed with hot dilute sodium hydroxide solution,* the dark brown extract neutralised with acid, and when cold the deposited indigo-brown is collected and weighed, the filtrate B being reserved. The filtrates A and B are then extracted with pure ether, the solution washed with water, and then evaporated, and the weight of this residue added to that of the main bulk. A defect in the method of indigo-brown analysis is the occasional presence in samples of Java indigo and other indigos prepared from the *I. arrecta* of indigo-yellow or kæmpferol (Trans., 1907, **91**, 435), because this substance is soluble in pyridine and in alkaline solutions, and is reprecipitated from the latter by means of acid. A search for this product in the samples under examination indicated that in the case of the Java varieties it was present to the extent of not more than 0·2 per cent., and would thus not materially affect the results, that it was absent in the case of the Coventry indigo, and that merely a trace was present in the new product from Bengal. As is well known, the Indian manufacturers are now employing the Java or Natal plant (*I. arrecta*) in place of the *I. sumatrana*, and the Bengal sample referred to above, and which was kindly procured for us by Mr. Oliver Marsden, of Leeds, was known to have been prepared from the first-named plant. An analysis carried out by the tetrasulphonate process indicated 68·3 of colouring matter.

Indigo-Brown in various Indigos (air dried).

Java indigo, new process, hot water.	Java indigo, new process, cold water.	Java indigo, ordinary process.	Coventry process, indigo.	New Bengal indigo.
5·4	5·2	4·15	8·7	9·60

It is therefore evident that Java indigos contain approximately one-half the indigo-brown which is present in the newest Indian variety, and a point which can only arise from details of manufacture. In an earlier investigation (Trans., 1907, **91**, 279), the amount of crude pyridine extract obtained from a mixture of numerous samples of Bengal indigo which had been prepared from the *I. sumatrana* worked out to 14 per cent., and although this mixture of samples without doubt contained considerably more indigo-brown than that contained in the new Bengal product just referred to, this value is somewhat too high for direct comparison, as it also includes, as was demonstrated at the time, some quantity of mineral matter. There is the strongest reason to regard indigo-brown as a waste product of the manufacture, and this has recently received considerable support from the isolation of a closely similar, if not identical, compound from the mixture of substances produced by the decomposition of indoxylic acid (Trans., 1909, **95**, 847).

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* 1 per cent.

It has been pointed out by one of us (Bloxam, *loc. cit.*) that when Bengal indigo has been freed from indigo gluten by means of dilute sulphuric acid, and the residue is then extracted with hot pyridine, it is only possible in this way to prepare an indigotin of about 91 per cent. purity. That this arose to some extent from obstinately retained mineral matter and plant debris was evident, but, on the other hand, the deficiency could not be entirely accounted for in this way. Further experiment now indicates that most indigos contain a small percentage of a brown impurity, insoluble in pyridine, and apparently in all solvents, but which dissolves to some extent in alkali to form a blackish-brown solution. On sulphonating, for instance, an indigo which has been purified by means of acid and pyridine with ordinary sulphuric acid, or, indeed, any commercial indigo, this compound is not attacked, and when the product is diluted with water it is precipitated apparently unchanged. In the analytical method described by Rawson (*J. Soc. Chem. Ind.*, 1899, **18**, 251), this brown material, at least in part, consists of the impurity which is carried down by a precipitation of barium sulphate in the liquid. As no data are available, it is useless to speculate as to the origin of this product, although its general characteristics suggest that it is allied to indigo-brown.

The Analysis of Indigo by the Pyridine Method.

For the accurate estimate of ordinary indigo it is now well recognised that it is necessary to eliminate the impurities which accompany the colouring matter, previous to or after the sulphonation process, and before the actual titration, because the sulphonation products of indigo-brown, and to a special degree those of indigo gluten, readily reduce the permanganate. These difficulties are avoided by the employment of the "tetrasulphonate" process, a full description of which is given by one of us elsewhere (Bloxam, *loc. cit.*). There could apparently be no doubt that by adopting the pyridine extraction method of analysis as above described, and by which a gradual elimination of the impurities is effected, an accurate estimation of indigo apart from the question of indirubin could be carried out, and the point was interesting as involving a further test of the trustworthiness of the tetrasulphonate process.

For the purpose of experiment a sample of Bengal indigo, containing but a trace of indirubin, was employed, and the procedure was exactly similar to that given above. For the analysis both by this and the tetrasulphonate method, duplicate titrations were carried out in each case with potassium permanganate and titanium chloride:

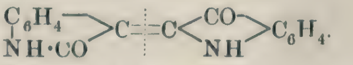
Pyridine method ……………	$KMnO_4$ = 60·27 per cent. $TiCl_3$ = 60·13 ,,	Mean = 60·20.
Tetrasulphonate method ……	$KMnO_4$ = 60·49 per cent. $TiCl_3$ = 60·05 ,,	Mean = 60·27.

The results given by the two methods thus harmonise remarkably, and this was to be anticipated on account of the numerous proofs which have been previously given by one of us (*loc. cit.*) as to the accuracy of the tetrasulphonate method.

Finally, it will no doubt be quite possible to analyse indigo with fair accuracy according to the pyridine method, by means of the Duboscq tintometer alone, but the employment of this process for practical purposes, with regard to indigo more or less free from indirubin, is not suggested on account of the somewhat lengthy operations involved.

The Effect of Indirubin in the Dyeing Operation.

In regard to the advantage or otherwise of the presence of indirubin in indigo, there has been considerable difference of opinion, and this still exists to some extent among dyers at the present time. According to Rawson and Knecht (*J. Soc. Dyers*, 1888, **4**), and also to Hummel (*ibid.*), indirubin is a valuable dyestuff, and is extremely fast to light. Matthews (*J. Soc. Chem. Ind.*, 1902, **21**, 222), however, points out that, in addition to other disadvantages, indirubin requires for reduction a much stronger reagent than indigotin, and that as a result the greater part of this dyestuff is not attacked in the indigo vat, but settles down to the bottom of the receptacle. Fasal (*Mitt. K. Tech. Gew.-Mus. Wien.*, 1895, **11**, 307) found that the shade of colour given by an indirubin vat became bluer from day to day, and that ultimately a pure indigo blue was produced. This change of tinctorial property was shown by this author to be due to the further reduction of leucoindirubin with the formation of indoxyl, and that this was oxidised on the fabric to indigotin. A more recent investigation of the reaction by one of us (Proc., 1909, **25**, 127) indicates that, in addition to indoxyl, oxindol is simultaneously produced, and that this should be the case is readily understood from the formula of indirubin itself:



$$\begin{array}{l}C_6H_4\\ \vert\\ NH\cdot CO\end{array}\!\!>C{=}{=}C<\!\!\begin{array}{l}CO\\ NH\end{array}\!\!>C_6H_4.$$

It therefore is evident that indirubin possesses little value as a vat dyestuff, and its presence in indigo cannot be considered of advantage, because it ultimately produces not more than one-half of its weight of indigotin.

On the other hand, indirubindisulphonic acid is, according to Fasol (*loc. cit.*) and also to Rawson and Knecht (*loc. cit.*), a useful dyestuff, and gives colours much faster to light than the corresponding indigo extract, which is sodium indigotindisulphonate.

The statement of Bergtheil (*Report of the Indigo Research Station*, Sirsiah, 1906), "Preliminary examination . . . has shown decisively that there is more than one red body in most commercial indigos," cannot be correct, because in all indigos at present experimented with in this and other investigations, no red substance other than indirubin has been detected.

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CXXXVI.—*The Relative Influence of the Ketonic and Ethenoid Linkings on Refractive Power.*

By IDA SMEDLEY.

THE exaltation in refractive power produced by the conjugation of unsaturated radicles, both with the carbonyl and with groups containing an ethenoid linking, has been discussed by several observers (Gladstone, *Proc. Roy. Soc.*, 1881, **31**, 327; Brühl, *Ber.*, 1907, **40**, 892; Perkin, Trans., 1907, **91**, 806; Smedley, Trans., 1908, **93**, 372; 1909, **95**, 218); it seemed possible, however, that the results already obtained might be somewhat simplified by making a quantitative comparison of the effect produced on the refractive power by the ketonic * and ethenoid linkings respectively under various conditions of conjugation.

If the exaltation of refractive power, produced by the mutual conjugation of groups containing the ethenoid linking, were the same as that produced by the conjugation of such groups with the carbonyl radicle, there should be a constant difference between the molecular refractions of any two compounds containing respectively the groups $C{:}CH_2$ and $C{:}O$, but otherwise similarly constituted.

It will be seen from the accompanying table that when placed at one end of a chain of conjugated unsaturated groups, the increment in refractive power when a $>C{:}CH_2$ group is substituted for a $>C{:}O$ group varies only between the limits 3·8 and 4·8, although the number of unsaturated groups entering into conjugation changes considerably.

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* The phrase "ketonic linking" is used in this paper to represent the double linking in the group $C{:}O$, whether the latter is present in an aldehydic or carboxylic group.

Table showing Increments in Refractive Power on replacing $C{:}O$ *by* $C{:}CH_2$.

Name.	Formula.	M_a.	Increment.	Observer.
Formaldehyde	$H_2C{:}O$	6·96	—	Estimated *
Ethylene	$H_2C{:}CH_2$	10·77	3·81	Liveing and Dewar
Acetone	$Me_2C{:}O$	16·05	—	Brühl
*iso*Butylene	$Me_2C{:}CH_2$	19·91	3·86	Estimated †
Ethylideneacetone	$Me\cdot\overset{H}{C}{:}\overset{H}{C}\cdot\overset{Me}{C}{:}O$	25·53	—	Estimated ‡ (1)
Dimethylbutadiene	$Me\cdot\overset{H}{C}{:}\overset{H}{C}\cdot\overset{H}{C}{:}CH$	30·38	4·85	Brühl
Maleic dialdehyde	$O{:}\overset{H}{C}\cdot\overset{H}{C}{:}\overset{H}{C}\cdot\overset{H}{C}{:}O$	21·08	—	Estimated ‖
Hexatriene	$H_2C{:}\overset{H}{C}\cdot\overset{H}{C}{:}\overset{H}{C}\cdot\overset{H}{C}{:}CH_2$	30·58	9·5/2 = 4·75	Perkin
Benzaldehyde	$Ph\cdot\overset{H}{C}{:}O$	31·77	—	Brühl
Styrene	$Ph\cdot\overset{H}{C}{:}CH_2$	35·98	4·21	,,
Benzophenone	$Ph_2C{:}O$	56·20	—	Eykmann
as-Diphenylethylene	$Ph_2C{:}CH_2$	60·10	3·90	,,
Cinnamaldehyde	$Ph\cdot\overset{H}{C}{:}\overset{H}{C}\cdot\overset{H}{C}{:}O$	43·51	—	Brühl
Phenylbutadiene	$Ph\cdot\overset{H}{C}{:}\overset{H}{C}\cdot\overset{H}{C}{:}CH_2$	48·00	4 49	Klages
Benzylideneacetone	$Ph\cdot\overset{H}{C}{:}\overset{H}{C}\cdot\overset{Me}{C}{:}O$	48·54	—	See p. 1482
Phenylmethylbutadiene	$Ph\cdot\overset{H}{C}{:}\overset{H}{C}.\overset{H}{C}{:}CHMe$	52·61	4·07	Klages

* M. Acetaldehyde .... 11·50
CH₂ in aldehyde series ... 4·54
∴ M. Formaldehyde ...... 6·96

† M. Ethylene .... 10·77
2 × CH₂ increment .... 9·14
∴ M. *iso*Butylene............ 19·91

‡ M. Mesityl oxide .... 30·13
CH₂ in ketone series ...... 4·60
∴ M. Ethylideneacetone... 25·53

‖ M. Maleic acid .... 23·94
2(Me·CO₂H − Me·CHO)... 2·86
∴ M. Maleic dialdehyde ... 21·08

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[1] The molecular refraction for the sodium line is found to be 25·78 (Auwers and Eisenlohr, *Ber.*, 1910, **43**, 817).

If now a comparison is made of the refraction increments obtained on substituting an ethenoid for a ketonic linking when it occurs, not at the end of a series of unsaturated hydrocarbon radicles, but in the middle of such a chain, much greater differences are observed.

Name.	Formula.	M_α.	Increment.	Observer.
Stilbene	$Ph\cdot\overset{H}{C}:\overset{H}{C}\cdot Ph$	65·65	—	Chilesotti
Benzophenone	$Ph\cdot\overset{O}{C}\cdot Ph$	56·20	9·45	Eykmann
Diphenylbutadiene	$Ph\cdot\overset{H}{C}:\overset{H}{C}\cdot\overset{H}{C}:\overset{H}{C}\cdot Ph$	82·9	—	Smedley
Benzylideneacetophenone	$Ph\cdot\overset{H}{C}:\overset{H}{C}\cdot\overset{O}{C}\cdot Ph$	70·55	11·35	P. 1482
Diphenylhexatriene	$Ph\cdot\overset{H}{C}:\overset{H}{C}\cdot\overset{H}{C}:\overset{H}{C}\cdot\overset{H}{C}:\overset{H}{C}\cdot Ph$	100·9	—	Smedley
Cinnamylideneacetophenone	$Ph\cdot\overset{H}{C}:\overset{H}{C}\cdot\overset{H}{C}:\overset{H}{C}\cdot\overset{O}{C}\cdot Ph$	87·6	13·3	P. 1483
Dibenzylideneacetone	$Ph\cdot\overset{H}{C}:\overset{H}{C}\cdot\overset{O}{C}\cdot\overset{H}{C}:\overset{H}{C}\cdot Ph$	84·0	16·9	P. 1483

When a carbonyl group is interposed in a chain of contiguous ethenoid groups, the exaltation of the refractive power is so much diminished that the increase in the molecular refraction of the compound produced by the addition of the carbonyl group may fall to 1 unit, as shown in the following table, a value much below that assigned to the same group in saturatel aliphatic compounds (4·7 units). This may perhaps be regarded as evidence in favour of the view that in a chain of contiguous ethenoid linkings the effect of each unsaturated group is not confined to the adjacent groups, but is transmitted along the whole chain, increasing the refractive effect of each link (compare Smedley, Trans., 1908, **93**, 372).

Table showing the Effect on Refractive Power of introducing a Carbonyl Group into Aromatic Hydrocarbons.

(Refraction value of CO in fatty compounds = 4·70.)

		M_α.	Increment.
Benzophenone	Ph·CO·Ph	56·20	—
Diphenyl	Ph·Ph	51·93	4·27
Benzylideneacetophenone	$Ph\cdot\overset{H}{C}:\overset{H}{C}\cdot\overset{O}{C}\cdot Ph$	70·55	—
Stilbene	$Ph\cdot\overset{H}{C}:\overset{H}{C}\cdot Ph$	65·65	4·9
Cinnamylideneacetophenone	$Ph\cdot\overset{H}{C}:\overset{H}{C}\cdot\overset{H}{C}:\overset{H}{C}\cdot\overset{O}{C}\cdot Ph$	87·6	—
Diphenylbutadiene	$Ph\cdot\overset{H}{C}:\overset{H}{C}\cdot\overset{H}{C}:\overset{H}{C}\cdot Ph$	82·9	4·7
Dibenzylideneacetone	$Ph\cdot\overset{H}{C}:\overset{H}{C}\cdot\overset{O}{C}\cdot\overset{H}{C}:\overset{H}{C}\cdot Ph$	84·0	—
Diphenylbutadiene	$Ph\cdot\overset{H}{C}:\overset{H}{C}\cdot\overset{H}{C}:\overset{H}{C}\cdot Ph$	82·9	1·1
Cinnamylidenebenzylideneacetone	$Ph\cdot\overset{H}{C}:\overset{H}{C}\cdot\overset{H}{C}:\overset{H}{C}\cdot\overset{O}{C}\cdot\overset{H}{C}:\overset{H}{C}\cdot Ph$	102·7	—

Refraction value of CO in fatty compounds = 4·70 (*continued*).

		M_a.	Increment.
Diphenylhexatriene	$\mathrm{Ph{\cdot}\overset{H}{\dot{C}}{:}\overset{H}{\dot{C}}{\cdot}\overset{H}{\dot{C}}{:}\overset{H}{\dot{C}}{\cdot}\overset{H}{\dot{C}}{:}\overset{H}{\dot{C}}{\cdot}Ph}$	100·9	1·8
Acetophenone	$\mathrm{Ph{\cdot}CO{\cdot}Me}$	36·00	—
Toluene	$\mathrm{Ph{\cdot}Me}$	30·80	5·2
Cinnamaldehyde	$\mathrm{Ph{\cdot}\overset{H}{\dot{C}}{:}\overset{H}{\dot{C}}{\cdot}\overset{O}{\ddot{C}}H}$	43·51	—
Styrene	$\mathrm{Ph{\cdot}\overset{H}{\dot{C}}{:}\overset{H}{\dot{C}}H}$	35·98	7·53
Cinnamylideneacetone	$\mathrm{Ph{\cdot}\overset{H}{\dot{C}}{:}\overset{H}{\dot{C}}{\cdot}\overset{H}{\dot{C}}{:}\overset{H}{\dot{C}}{\cdot}\overset{O}{\ddot{C}}{\cdot}Me}$	64·2	—
Phenylmethylbutadiene	$\mathrm{Ph{\cdot}\overset{H}{\dot{C}}{:}\overset{H}{\dot{C}}{\cdot}\overset{H}{\dot{C}}{:}\overset{H}{\dot{C}}{\cdot}Me}$	52·6	11·6

A comparison of the two isomeric diphenylethylenes with benzophenone suggests that the effect of the ketonic linking still resembles that of the ethenoid linking, but when interposed between two unsaturated radicles, the ketonic must be compared with an ethenoid linking which itself joins a side-chain:

		M_a.			M_a.
Stilbene	$\mathrm{Ph{\cdot}\overset{H}{\dot{C}}{:}\overset{H}{\dot{C}}{\cdot}Ph}$	65·65	Diphenylethylene,	$\mathrm{Ph{\cdot}\overset{CH_2}{\ddot{C}}{\cdot}Ph}$	60·10
Benzophenone,	$\mathrm{Ph{\cdot}\overset{O}{\ddot{C}}{\cdot}Ph}$	56·20	Benzophenone,	$\mathrm{Ph{\cdot}\overset{O}{\ddot{C}}{\cdot}Ph}$	56·20
		9·45			3·9

The difference in the refractive power of the isomeric cinnamylideneacetophenone and dibenzylideneacetone is well marked; the molecular refraction of the compound containing the longer chain of conjugated unsaturated linkings exceeds by 3·6 units the refraction value of the symmetrically arranged isomeride.

Since writing the above, my attention has been called to a paper published by Auwers and Eisenlohr (*Ber.*, 1910, **43**, 806), in which the effect of the conjugation of unsaturated groups is discussed. These authors quote the statement of Brühl (*Ber.*, 1907, **40**, 1153) that the group $\mathrm{{\cdot}\overset{O}{\ddot{C}}{\cdot}\overset{O}{\ddot{C}}{\cdot}}$ does not produce exaltation of refraction; the present author has previously pointed out that in aromatic compounds this group produces a marked effect on refraction (compare Armstrong and Robertson, Trans., 1905, **87**, 1275; Smedley, 1909, **95**, 221), and has suggested that the peculiar influence of this group is to be attributed rather to the mutual influence of the oxygen atoms.

Auwers and Eisenlohr draw the conclusion that the substitution of an alkyloxy-group for a hydrogen atom decreases the exaltation of refractive power produced by conjugation, and contend further that a more marked reduction is produced by substituting an alkyloxy- than by an alkyl or hydroxy-group. There appears to be an error in the figure quoted for the molecular refraction of cinnamaldehyde. The value for the sodium line calculated from Brühl's data, to which reference is made, is 44·14 instead of 45·21, a difference which removes one instance of the three quoted. There is also always possibility of error when values are calculated from the atomic refractions, and when, for instance, the value for the carbonyl group is assumed to be identical in aldehydes and ketones; instead of using the method adopted by Auwers, the following basis of comparison may be employed, which is independent of calculated values for the atomic refractions.

	M.R.$_D$.	Difference, R·COMe − R·COH.
Acetone	16·13	
Acetaldehyde	11·56	
		4·57
Ethylideneacetone ..	25·78	
Crotonaldehyde... ...	21·47	
		4·31
Acetophenone	36·34	
Benzaldehyde	32·02	
		4·32
Benzylideneacetone...	48·41	
Cinnamaldehyde ...	44·14	
		4·27

	M.R$_D$.	Difference, R·CO·OH − R·COH.
Acetic acid	12·99	
Acetaldehyde	11·56	
		1·43
Butyric acid............	22·16	
Butaldehyde	20·62	
		1·54
Crotonic acid *	22·63	
Crotonaldehyde	21·47	
		1·16

* Auwers and Eisenlohr (*Ber.*, 1910, **43**, 817). The value given for crotonic acid is for the α-line.

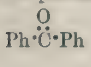
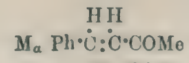
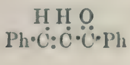
	M.R.$_D$.	Difference, R·CO·OMe − R·COH.
Methyl acetate	18·11	
Acetaldehyde	11·56	
		6·55
Methyl butyrate	26·91	
Butaldehyde	20·62	
		6·29
Methyl benzoate	37·80	
Benzaldehyde	32·02	
		5·78
Methyl cinnamate ...	49·31	
Cinnamaldehyde ...	44·14	
		5·17

	M.R.$_D$.	Difference, R·CO·OMe − R·COH.
Ethyl acetate	22·24	
Acetaldehyde	11·56	
		10·68
Ethyl butyrate	31·35	
Butaldehyde	20·62	
		10·73
Ethyl crotonate	31·68	
Crotonaldehyde	21·47	
		10·21
Ethyl benzoate	42·55	
Benzaldehyde	32·02	
		10·53
Ethyl cinnamate......	54·19	
Cinnamaldehyde	44·14	
		10·05

A study of the above table shows that the difference in molecular refraction between an aldehyde and the corresponding methyl ketone varies very slightly in saturated and unsaturated compounds. The diminution which takes place in this difference in the unsaturated compounds quoted is so slight that but little importance can be attached to it. The distinction drawn by Auwers and Eisenlohr between the influence of the hydroxyl and that of the alkyloxy-groups does not appear to be warranted by the evidence given. The difference between the molecular refractions of crotonic acid and aldehyde is slightly lower than the corresponding difference in the aliphatic series; similarly, there is a decrease in the increment of the molecular refraction of crotonic ester over that of crotonaldehyde. This diminution is intensified in the cinnamic series, but the value for cinnamic acid, which has only been examined in solution, is excluded from the table; and the numbers for the crotonic series alone do not appear to warrant any distinction being made between the behaviour of the acid and its esters.

It is probable that the diminished effect produced by the conjugation of the carbonyl group in acids and esters, as compared with that in ketones and aldehydes, may be attributed to the mutual effect of the two oxygen atoms whereby the residual affinity of the carbonyl oxygen is lessened (Trans., 1909, **95**, 231).

Auwers and Eisenlohr also discuss the question of "crossed double bonds," and are led to the conclusion that if three "crossed double bonds" are present, the exaltation of refractive power is much slighter than when three conjugated double bonds are present in an open chain, and remains below that of the related substance containing only two conjugated double bonds. The present author's results show that when the number of unsaturated groups is considerably increased, the two side-chains terminating in the same unsaturated group do have marked effect on each other in exalting refractive power.

Substance.	(Observed) M_α.	Calculated Value.		Difference.
Benzophenone,		M_α Ph·COMe	36·00	
 $\mathrm{Ph{\cdot}\overset{O}{\ddot{C}}{\cdot}Ph}$		Ph·COMe	36·00	
			72·00	
		− M_α $COMe_2$	16·05	
	56·20		55·95	0·25
Benzylideneacetophenone,		 $\mathrm{M_\alpha\ Ph{\cdot}\overset{H}{\dot{C}}{:}\overset{H}{\dot{C}}{\cdot}COMe}$	48·54	
 $\mathrm{Ph{\cdot}\overset{H}{\dot{C}}{:}\overset{H}{\dot{C}}{\cdot}\overset{O}{\ddot{C}}{\cdot}Ph}$		Ph·COMe	36·00	
			84·54	
		− M_α $COMe_2$	16·05	
	70·55		68·49	2·1

Substance.	(Observed) M_{α}.	Calculated Value.		Difference.
Dibenzylideneacetone,		$M_{\alpha}\ \mathrm{Ph\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot COMe}$	48·54	
$\mathrm{Ph\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot\overset{O}{\ddot{C}}\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot Ph}$		$\mathrm{Ph\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot COMe}$	48·54	
			97·08	
		$-M_{\alpha}\ \mathrm{COMe_2}$	16·05	
	84·00		81·03	3·0
Cinnamylideneacetophenone,		$M_{\alpha}\ \mathrm{Ph\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot COMe}$	64·19	
$\mathrm{Ph\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot\overset{O}{\ddot{C}}\cdot Ph}$		$\mathrm{Ph\cdot COMe}$	36·00	
			100·19	
		$-M_{\alpha}\ \mathrm{COMe_2}$	16·05	
	87·59		84·14	3·45
Cinnamylidenebenzylidene-acetone,		$M_{\alpha}\ \mathrm{Ph\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot COMe}$	64·19	
$\mathrm{Ph\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot\overset{O}{\ddot{C}}\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}Ph}$		$\mathrm{Ph\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot COMe}$	48·54	
			112·73	
		$-M_{\alpha}\ \mathrm{COMe_2}$	16·05	
	102·7		96·68	6·0
Dicinnamylideneacetone,		$M_{\alpha}\ \mathrm{Ph\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot COMe}$	64·19	
$\mathrm{Ph\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot\overset{O}{\ddot{C}}\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot Ph}$		$\mathrm{Ph\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot\overset{H}{\dot{C}}:\overset{H}{\dot{C}}\cdot COMe}$	64·19	
			128·38	
		$-M_{\alpha}\ \mathrm{COMe_2}$	16·05	
	121·5		112·33	9·2

In the accompanying table, a method of calculation is used in which the exaltation effect of each side-chain of groups containing ethenoid linkings with the contiguous carbonyl radicle is separately allowed for and the minimum value of one carbonyl group subtracted. If the two side-chains of groups containing ethenoid linkings have no effect on each other through the carbonyl radicle, the values calculated should be higher than that actually observed, since the minimum value for a carbonyl group has been subtracted. Yet as the number of groups conjugated is increased in each chain, the observed value becomes markedly greater than that calculated; in some manner therefore the two chains of unsaturated radicles present on either side of, and each terminating in, the same carbonyl group are able to influence each other. It is a point of some interest whether the $>CH_2$ group acts similarly to the >CO group, or whether it is only when separated by an unsaturated group that this imperfect screening effect is present. At present sufficient data are not available to enable this point to be decided with certainty. It may be that the exaltation of refractive power is caused by the conjugation of the chain of groups containing ethenoid linkings with a carbonyl group, the influence of which has already been exalted by the second chain of unsaturated groups to which it is contiguous, or it may be that the screening effect is not connected with the unsaturated character of the group interposed. The determinations of magnetic rotation led Perkin (Trans., 1896, **69**, 1091) to the conclusion that the screening effect of the carbonyl is greater than that of the methylene group. There are, however, considerable differences in the relative influence of the CO and CH_2 groups on rotation and refraction. The association of carbonyl with the phenyl nucleus has a reducing influence on the rotation value of the phenyl group—a result which appears to be entirely at variance with the exaltation of refractive power produced by the conjugation of the same groups; the molecular refraction of benzaldehyde is greater than that of toluene, but the magnetic rotation of the former is less.

EXPERIMENTAL.

Determinations of Refractive Power.

(1) *Benzylideneacetone* in chloroform solution. This substance was obtained from Kahlbaum, and was recrystallised from alcohol. Melting point 41—42°:

Percentage strength of solution.	M_α.	M_β.	M_γ.
9·6273	48·75	51·60	53·65
8·1535	48·27	51·06	53·80
6·8712	48·56	51·33	54·07
14·6205	48·50	51·32	53·63
Mean......	48·52 *	51·33	53·79

$M_\beta - M_\alpha = 2·81$; $M_\gamma - M_\alpha = 5·27$.

* Auwers and Eisenlohr (*Ber.*, 1910, **43**, 817) find, for the pure substance, $M_D = 48·41$.

(2) *Benzylideneacetophenone* in chloroform solution. Melting point 58°:

Percentage strength of solution.	M_α.	M_β.	M_γ.
5·6935	70·60	75·40	80·36
4·6774	70·42	75·12	81·04
10·5939	70·43	75·30	79·33
Mean......	70·48	75·27	80·25

$M_\beta - M_\alpha = 4·79$; $M_\gamma - M_\alpha = 9·77$.

(3) *Cinnamylideneacetone* (Diehl, *Ber.*, 1885, **18**, 2321) in chloroform solution. Melting point 68—69°. The product must be recrystallised before using, as it decomposes on keeping, forming an oily residue containing both acetic acid and cinnamaldehyde:

Percentage strength of solution.	M_α.	M_β.
8·0070	64·24	70·92
5·8710	64·27	70·79
6·4876	63·96	70·65
3·4655	64·24	71·07
0·8150	64·58	—
11·8473	63·77	70·38
Mean	64·19	70·76

$M_\beta - M_\alpha = 6·37$.

(4) *Dibenzylideneacetone* in chloroform solution. The specimen used was obtained from Kahlbaum; when crystallised from alcohol it melted at 111—112°:

Percentage strength of solution.	M_α.	M_β.
12·0201	83·71	91·68
12·8012	83·81	91·70
11·8836	84·20	92·21
4·1027	84·46	93·08
Mean	84·04	92·17

$M_\beta - M_\alpha = 8·13$.

(5) *Cinnamylideneacetophenone* (Scholtz, *Ber.*, 1895, **28**, 1730) in chloroform solution. Melting point 102°:

Percentage strength of solution.	M_α.	M_β.
5·7299	87·53	98·53
5·7298	87·25	98·10
17·4681	87·72	—
5·2641	87·85	97·87
Mean	87·59	98·17

$M_\beta - M_\alpha = 10·58$.

(6) *Cinnamylidenebenzylideneacetone* in chloroform solution. This substance, previously prepared by condensing cinnamylideneacetone with benzaldehyde (Scholtz, *Ber.*, 1896, **29**, 614), was obtained as follows. 6·6 Grams of cinnamaldehyde and 7·3 grams of benzylideneacetone were dissolved in 150 grams of ethyl alcohol, and 200 c.c. of water and 20 grams of 10 per cent. aqueous sodium hydroxide were added. After a few minutes the milky solution became intensely yellow, and an oil separated, which, after twenty-four hours, solidified to a mass of yellow crystals. These, when

recrystallised from a mixture of chloroform and alcohol, melted at 109°:

Percentage strength of solution.	M_a.
5·1344	102·69

(7) *Dicinnamylideneacetone* (Diehl, *Ber.*, 1885, **18**, 2325) in chloroform solution. The yellow needles were recrystallised from acetone, and melted at 142°:

Percentage strength of solution.	M_a.
0·8841	121·79
2·7077	121·65
2·2509	122·46
7·1955	120·23

Much of the expense of this research has been met by a grant from the Research Fund Committee of the Chemical Society.

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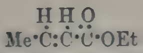
CXXXVII.—*The Constitution of the β-Diketones.*

By IDA SMEDLEY.

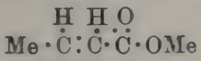
THE investigation both of the magnetic rotation and of the molecular refraction of ethyl acetoacetate and its alkyl derivatives by Perkin (Trans., 1892, **61**, 800) and Brühl (*Ber.*, 1892, **25**, 369; *J. pr. Chem.*, 1894, [ii], **50**, 131) led to the conclusion that these compounds were ketonic in structure. The study of the aliphatic β-diketones by the same observers showed that their physical constants did not accord with a diketonic structure. To acetylacetone a di-enolic structure was ascribed (Brühl, *J. pr. Chem.*, 1894, [ii], **50**, 192); the methyl derivative was regarded as keto-enolic, and the ethyl derivative as a true diketone.

In the light of our present knowledge as to the influence of the conjugation of unsaturated groups on the physical constants of compounds, it becomes necessary to revise the conclusions previously drawn as to the structure of the aliphatic β-diketones.

If the increment in refraction produced by the conjugation of an ethenoid with a carbonyl group be introduced, the calculated value for the molecular refraction of acetylacetone in its keto-enolic form agrees well with that observed. The particular type of conjugation occurring in the keto-enolic form of acetylacetone is found in ethyl crotonate, the refraction of which has been measured (Brühl, *loc. cit.*), and may therefore serve as a standard:

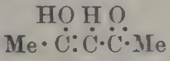
	M.R.$_\alpha$ (observed).
Ethyl crotonate,  $Me\cdot\overset{H}{C}:\overset{H}{C}\cdot\overset{O}{C}\cdot OEt$	31·5
The difference between the refraction values of corresponding ethyl and methyl esters varies from	4·5 to 4·1
Difference	27·0 to 27·4

The value for methyl crotonate may therefore be assumed to lie between 27·0 and 27·4. The molecular refractions of methyl crotonate (I) and the keto-enolic form of acetylacetone (II) should



$Me\cdot\overset{H}{C}:\overset{H}{C}\cdot\overset{O}{C}\cdot OMe$

(I.)



$Me\cdot\overset{HO}{C}:\overset{H}{C}\cdot\overset{O}{C}\cdot Me$

(II.)

closely resemble each other; the value actually observed for acetylacetone is 27·3 (Perkin) or 27·4 (Brühl). The evidence from refractive power accords therefore with the keto-enolic structure for acetylacetone, and it is unnecessary to assume the existence of the di-enolic form.

The substitution of a methyl group for one of the hydrogen atoms in acetylacetone is accompanied by an increase of 3·35 units in the observed molecular refraction (Perkin, *loc. cit.*):

	$M_\alpha.\left(\frac{M.(\mu_\alpha^2-1)}{d\,(\mu_\alpha^2+2)}\right).$
Methylacetylacetone	30·64
Acetylacetone	27·29
	3·35

A similar substitution in a compound where no change of constitution is probable is accompanied by an increase of approximately 4·5 units; the abnormally small increment in refraction which is observed when the methyl group is introduced into acetylacetone makes it appear probable that there is a difference of structure between acetylacetone and its methyl derivative.

The value actually observed for methylacetylacetone is intermediate between those required for the diketonic and keto-enolic forms respectively:

		M.R.$_\alpha$.
Value estimated for the keto-enolic form (observed value for ethyl crotonate)		31·5
Value estimated for the diketonic form:		
M.R.$_\alpha$ methyl ethyl ketone	20·57	
M.R.$_\alpha$ acetone	16·05	
	36·6	
Less M.R.$_\alpha$ methane	6·6	
	30·0	30·0
Value observed for methylacetylacetone		30·75

A study of the magnetic rotatory power of the alkyl derivatives of acetylacetone led Perkin to the conclusion that the ethyl compound was a diketone, and the methyl derivative was intermediate between ethylacetylacetone and the unalkylated compound. Alkylation tended to produce the ketonic form. The same rule appears to apply to the refractive power.

The order of the increment caused by the conjugation of unsaturated groups becomes so much magnified in aromatic substances that deductions as to constitution may more safely be drawn, and it was therefore a matter of some interest to investigate the refractive power of the aromatic β-diketones.

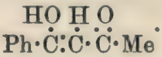
Benzoylacetone.

The magnetic rotation of this compound was determined by Perkin, who found that it approached most nearly to that required by the hydroxy-ketonic formula, being 1·051 units in excess of that calculated:

Magnetic Rotation.

Calculated for hydroxyketonic formula	17·731
Observed	18·782

In his investigation of the magnetic rotation of cinnamyl compounds, Perkin (Trans., 1896, **69**, 1145) showed that all gave values higher than those calculated. The increments show some variation: in the case of benzylideneacetone it reaches 1·489 (4·323—2·834), whilst for cinnamaldehyde it is 0·89 (3·724—2·834). The increment observed in the case of benzoylacetone agrees therefore with its representation by the formula

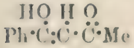


$$Ph\cdot\overset{HO}{\dot{C}}:\overset{H}{\dot{C}}\cdot\overset{O}{\ddot{C}}\cdot Me.$$

The molecular refraction now determined in chloroform solution is

$$M_{\alpha}=50\cdot3\,;\ M_{\gamma}-M_{\alpha}=5\cdot8.$$

A comparison of this value with that obtained for benzylideneacetone (this vol., p. 1482) shows that the observed value for benzoylacetone is in accordance with that required for a hydroxyl derivative of benzylideneacetone:

	M.R.$_{\alpha}$.	$M_{\gamma}-M_{\alpha}$.
Benzylideneacetone	48·5	5·3
Replacement of H by OH	1·5	—
 $Ph\cdot\overset{HO}{\dot{C}}:\overset{H}{\dot{C}}\cdot\overset{O}{\ddot{C}}\cdot Me$	50·0	5·3
Observed for benzoylacetone	50·3	5·8

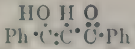
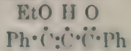
These results are within the limits of accuracy of the experimental method used.

Dibenzoylmethane.

The constitution of this substance was discussed by Wislicenus (*Annalen*, 1899, **308**, 219), who claimed to have isolated a diketonic form isomeric with the substance originally obtained by Baeyer and Perkin (*Ber.*, 1883, **16**, 2134), to which latter Wislicenus therefore ascribed a hydroxy-ketonic structure. Subsequently, Ruhemann and Watson (Trans., 1904, **85**, 456) showed that the compound described by Wislicenus was not isomeric with dibenzoylmethane, but was the ethoxy-derivative of benzylideneacetophenone.

Dibenzoylmethane, obtained by the condensation of ethyl benzoate and acetophenone, is generally pink or red in colour (possibly due to the presence of traces of an iron salt), and it is difficult completely to remove this colour by recrystallisation. If, however, the dibenzoylmethane is dissolved in cold concentrated sulphuric acid and reprecipitated by water, its melting point is unchanged (78°), but it is now pale yellow in colour, nor is this colour removed by repeated recrystallisation. The colour is interesting, because it closely resembles that of benzylideneacetophenone, whereas in the alkyl derivatives of dibenzoylmethane no yellow colour could be detected. The ethoxy-derivative of benzylideneacetophenone appeared also to be persistently yellow. So far therefore as the argument from colour is concerned, benzylideneacetophenone, its ethoxy-derivative, and dibenzoylmethane may be classed together as pale yellow compounds. The alkyl derivatives of dibenzoylmethane are, however, colourless.

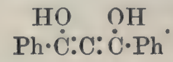
Refractive Power.—The values estimated for the hydroxy- and ethoxy-derivatives of benzylideneacetophenone, together with those observed for dibenzoylmethane and ethoxybenzylideneacetophenone, are as follows:

	M_α.	M_β.	M_γ.	M_α.	M_β.	M_γ.
Benzylideneacetophenone ……	70·4	75·3	79·3			
Replacement, H by OH ……… (Benzyl alcohol—toluene)	1·4	1·4	1·4			
Estimated value for  $Ph\cdot\overset{HO}{C}:\overset{H}{C}\cdot\overset{O}{C}\cdot Ph$ ………………… ….				71·8	76·7	80·7
Observed value for dibenzoylmethane …… . ……………				74·6	81·5	88·0
Difference ……… . …………. ..				2·8	4·8	7·3
Benzylideneacetophenone ……	70·4	75·3	79·3			
Replacement, H by OEt ………	10·6	10·7	10·8			
Estimated value for  $Ph\cdot\overset{EtO}{C}:\overset{H}{C}\cdot\overset{O}{C}\cdot Ph$ … . … . ……… …..				81·0	86·0	90·1
Observed value for ethoxybenzylideneacetophenone …				79·6	85·2	—
Difference …… . .. . …….				1·4	0·8	—

The differences between the observed and calculated values for ethoxybenzylideneacetophenone are within those allowed for the experimental error of the method used (2 per cent.), and there is no marked increase in dispersion. The increase in dispersion and the magnitude of the difference in the case of dibenzoylmethane are, however, beyond those which can be regarded as due to experimental error. The estimated value for the diketone would be obviously much less than that for the hydroxy-ketone:

$$[2M.R._{\alpha}\ Ph\cdot CO\cdot Me - M.R._{\alpha}\ CH_4 = 72{\cdot}0 - 6{\cdot}6 = 65{\cdot}4].$$

It was thought that a possible explanation might be found for the discrepancy by attributing a di-enolic structure to dibenzoylmethane, which would then be represented as an allene derivative,



$$Ph\cdot\overset{HO}{C}:C:\overset{OH}{C}\cdot Ph.$$

It was conceivable that if this represented the structure of dibenzoylmethane, its carboxyl derivative might show optical activity; the *p*-carbethoxyl derivative was prepared by condensing diethyl terephthalate with acetophenone in the presence of sodamide, and showed the red tinge characteristic of dibenzoylmethane; it melted at 98°. It was soluble in sodium hydroxide, and gave an intense red colour with ferric chloride. On hydrolysis, a pale yellow carboxyl compound, melting at 232°, was obtained. Its strychnine and cinchonine salts were prepared in a crystalline state from solution in methyl alcohol, but specimens of the acid prepared from successive fractions of the crystals obtained showed no trace of optical activity.

The refractive power of certain aliphatic allene derivatives was investigated by Brühl, who concluded that no exaltation of refractive power occurs such as accompanies the conjugation of two ethenoid linkings.

Tetraphenylallene was prepared by the distillation of barium diphenylacetate (Vorländer, *Ber.*, 1906, **39**, 1024), and its refractive power examined. In preparing this substance, a mixture of two hydrocarbons at once crystallised from the oily distillate as Vorländer described; these were separated, and on leaving the remaining oil for some weeks, large, transparent plates, identified as tetraphenylacetone, were also obtained. These melted at 27—28°; no oxime could be obtained by prolonged boiling with hydroxylamine solution; this is probably an instance of the action of steric hindrances.

Molecular Refraction estimated for Tetraphenylallene.

	M_{α}.	
2M.R.$_{\alpha}$ *as*-diphenylethylene, $Ph_2C:CH_2$. 2 × 60·1 =	120·2	
− M.R.$_{\alpha}$ CH_4	6·6	
		113·6
Observed value		117·7
Difference		4·1

Molecular Refraction estimated for Tetraphenylallene.

The exaltation produced is therefore very much less than when double bonds enter into conjugation (compare Trans., 1908, **93**, 372), and is insufficient to explain the high value found for the molecular refraction of dibenzoylmethane. From the data available, the calculated values for the di-enolic allene form and the hydroxy-ketonic form of dibenzoylmethane do not greatly differ.

Molecular Refraction estimated for Dihydroxydiphenylallene.

	M_α.	M_β.
M.R. tetraphenylallene............................	117·7	124·5
−2(M.R. $Ph_2C:CH_2$ − M.R. $Ph\cdot HC:CH_2$) ...	−48·2	−49·8
+2(OH − H)	+2·8	+2·8
	72·3	77·5
Observed value for dibenzoylmethane.........	74·6	81·5
[Estimated value for hydroxy-ketonic formula	71·8	76·7]

No evidence could therefore be obtained in favour of the existence of a di-enolic form of dibenzoylmethane. It is probable that dibenzoylmethane does exist in the hydroxy-ketonic form; a possible explanation of the abnormal refractive power may perhaps lie in the symmetry of the molecule and the consequent oscillation of a hydrogen between the two oxygen atoms. If this be so, the deviation should be less when substituents are introduced into one of the phenyl nuclei; but at present there is not sufficient evidence to show that the possibility of such an oscillation is attended with an exaltation of refractive power.

Alkyl Derivatives of Dibenzoylmethane.

The *αα*- and *ββ*-dibenzoylpropanes were prepared, and their refractive powers examined. The molecular refractions of both are best in accordance with the diketonic structure.

Molecular Refraction estimated for ββ-Dibenzoylpropane.

	M_α.	M_β.	M_γ.
M.R. [2Ph·CO·Me + ·C·]	74·4	—	77·91
Observed : *αα*-Dibenzoylpropane	74·98	78·40	79·37
ββ-Dibenzoylpropane	75·99	78·25	—

Action of Grignard's Reagent on the Aromatic β-Diketones.

The application of Hibbert and Sudborough's method for the determination of the number of hydroxyl groups present in the aromatic β-diketones by observing the volume of gas liberated when a known quantity of the substance is treated with excess of the Grignard reagent, gave results agreeing with the presence of one hydroxyl group in dibenzoylmethane and with a diketonic structure for dimethyldibenzoylmethane. In the case of benzoylacetone, the volume of gas evolved was about two-thirds of that required by theory for the hydroxy-ketonic structure.

A study of the products formed showed that ββ-dibenzoylpropane reacts with magnesium methyl iodide, forming the tertiary alcohol, $C_6H_5\cdot CO\cdot CMe_2\cdot CMe(OH)\cdot C_6H_5$. The chief product of the interaction of dibenzoylmethane and magnesium phenyl iodide was always the unchanged substance; a small amount of a pale yellow substance, melting at 89°, was obtained, analysis of which agreed with the formula $C(C_6H_5)_2{:}CH\cdot CO\cdot C_6H_5$.

EXPERIMENTAL.

Benzoylacetone.—This substance was obtained from Kahlbaum and recrystallised from alcohol. Its refractive power was examined in chloroform solution:

Percentage strength of solution.	M_α.	M_β.	M_γ.
10·459	50·28	53·52	56·05

Dibenzoylmethane.—The dibenzoylmethane used was prepared by the condensation of ethyl benzoate and acetophenone in dry ethereal solution under the influence of sodamide (Claisen, *Ber.*, 1905, **38**, 693). The sodium compound was decomposed by gradually adding it to glacial acetic acid, precipitating by the addition of water, and recrystallising from methyl alcohol and light petroleum. The crystals so obtained were always of a pink tinge, and melted at 78°.

Determination of refractive power in chloroform solution:

Percentage strength of solution.	M_α.	M_β.	M_γ.
3·2007	74·16	81·43	87·96
9·0754	74·56	81·45	—
3·0884	74·96	81·67	—
Mean	74·56	81·52	

Ethoxybenzylideneacetophenone.—The starting point in preparing this substance was dibenzylideneacetophenone (Ruhemann and Watson, Trans., 1904, **85**, 456); in brominating this, the dibromide described by Wislicenus, melting at 157—158°, was obtained, and in addition a stereoisomeric compound, melting at 112—113° (Proc., 1909, **25**, 259).

The pale yellow crystals of ethoxybenzylideneacetophenone melted at 78°; their refractive power was determined in chloroform solution:

Percentage strength of solution.	M_α.	M_β.
1·5710	79·95	85·16
3·0607	79·25	—

Preparation of p-*Carbethoxydibenzoylmethane.*—Twenty-two grams of diethyl terephthalate and 11 grams of acetophenone were dissolved in dry ether, and 8 grams of sodamide gradually added. The mixture was surrounded by ice and kept overnight. The insoluble sodium compound which separated was collected, and decomposed with ice and glacial acetic acid; the product, when recrystallised from methyl alcohol, melted at 97—98°. It was pink in colour, soluble in sodium hydroxide, and gave an intense red colour with ferric chloride:

0·0973 gave 0·2600 CO_2 and 0·044 H_2O. C = 72·88; H = 5·03.

$C_{18}H_{16}O_4$ requires C = 72·97; H = 5·40 per cent.

Hydrolysis.—Twenty grams of the carbethoxy-compound were dissolved in boiling alcohol, a 10 per cent. solution of alcoholic potash added, and the mixture warmed on a water-bath for from five to ten minutes. The yellow insoluble potassium salt which separated was dissolved in water, and the solution acidified with dilute hydrochloric acid. A pale yellow substance, melting at 225°, separated, which was very sparingly soluble in alcohol, but could be recrystallised from ethyl acetate or from glacial acetic acid; it melted at 232° when recrystallised from ethyl acetate.

Preparation of Tetraphenylacetone.—From the oily distillate obtained by distilling barium diphenylacetate (Vorländer and Siebert, *Ber.*, 1906, **39**, 1024) under a pressure of 10 mm., there separated white crystals, which on recrystallisation from alcohol melted at 166°, and consisted of tetraphenylallene. The melting point of successive crops of crystals was lower, and consisted of a mixture of the two hydrocarbons described by Vorländer. The oily residue was kept for some weeks, and eventually crystallised, large, transparent, tabular plates being formed at the surface of the liquid. These melted at 24—26°, and on recrystallisation from dilute alcohol at 27—28°:

0·1104 gave 0·3634 CO_2 and 0·0585 H_2O. C = 89·77; H = 5·79.

$C_{27}H_{22}O$ requires C = 89·50; H = 6·07 per cent.

This substance is therefore the tetraphenylacetone which Vorländer and Siebert assumed to be first formed in the reaction, but which they did not then succeed in isolating.

A solution heated on a water-bath for twelve hours with a large excess of hydroxylamine appeared unchanged; the original substance was recovered, and no oxime could be detected.

Refractive Power of Tetraphenylacetone.

Percentage of substance in chloroform solution.	M_α.	M_β.
4·3617	115·3	119·3

Refractive Power of Tetraphenylallene (m. p. 166°).

Percentage of substance in chloroform solution.	M_α.	M_β.	M_γ.
1·7290	117·91	124·97	128·29
2·1585	117·55	124·0	125·9

αα-Dibenzoylpropane.

This substance cannot be directly prepared from dibenzoylmethane by ethylation; it was obtained (Auger, *Ann. Chim. Phys.*, 1891, [vi], **22**, 351) by the action of aluminium chloride on a mixture of benzene and the dichloride of ethylmalonic acid, and the product purified by distillation under diminished pressure. The distillate remained for a long time as an oil which only gradually solidified after keeping for some days. It was purified by recrystallisation from alcohol and from petroleum, and eventually obtained in colourless needles, melting at 86—87°.

An attempt to prepare dibenzoylethane by condensing propiophenone and ethyl benzoate in dry ethereal solution in the presence of sodamide was not successful. An insoluble sodium compound is formed, which appears to be hydrolysed with extreme ease.

Refractive Power of αα-Dibenzoylpropane.

Percentage of subtance in chloroform solution.	M_α.	M_β.	M_γ.
3·5043	74·98	78·40	79 37

ββ-Dibenzoylpropane.

This was prepared by condensing the dichloride of dimethylmalonic acid with benzene in the presence of aluminium chloride.

One hundred grams of dimethylmalonic acid and 170 grams of thionyl chloride were heated from three to four hours on a water-bath, and the product then distilled under diminished pressure. Forty grams of the dichloride thus obtained were dissolved in 400 c.c. of benzene, and 60 grams of aluminium chloride gradually added. The mixture was kept overnight, and then heated for two hours on a water-bath. After distilling off the excess of benzene, the warm product was poured into water and extracted with ether. The excess of ether was evaporated and light petroleum added to the concentrated ethereal solution, when colourless needles separated. These, when recrystallised from light petroleum, melted at 99°, and gave no red coloration with ferric chloride:

0·1238 gave 0·3640 CO_2 and 0·0730 H_2O. C=80·19; H=6·55.

$C_{17}H_{16}O_2$ requires C=80·95; H=6·35 per cent.

Refractive Power of ββ-Dibenzoylpropane.

Percentage of substance in chloroform solution.	M_α.	M_β.
5·1545	75·99	78·25

Action of Grignard Reagent on ββ-Dibenzoylpropane.

To an ethereal solution of 1 gram of magnesium and 6 grams of methyl iodide, an ethereal solution of 5 grams of ββ-dibenzoylpropane was added. After keeping overnight, the product was decomposed, first with ice-water, and then with 30 per cent. sulphuric acid. The solution was extracted with ether, and the product distilled under diminished pressure.

A fraction boiling between 120° and 125°/55 mm. was obtained, which gave a red colour with ferric chloride:

0·0867 gave 0·2555 CO_2 and 0·0593 H_2O. C=80·3; H=7·6.

$C_{18}H_{20}O_2$ requires C=80·60; H=7·44 per cent.

The product is therefore the tertiary alcohol,

$C_6H_5{\cdot}CO{\cdot}CMe_2{\cdot}CMe(OH){\cdot}C_6H_5$.

Estimation of Hydroxyl Groups Present in the Aromatic β-Diketones.

A solution of magnesium methyl iodide in amyl ether was used as described by Hibbert and Sudborough (Trans., 1904, **85**, 933). This reagent, together with a weighed quantity of the substance, was introduced into a flask, and the volume of gas evolved measured in a nitrometer:

Substance.	Weight, gram.	Volume of gas evolved (N.T.P.) c.c.	Volume corresponding with presence of one hydroxyl group in the molecule. c.c.
ββ-Dibenzoylpropane	0·144	0·0	—
	0·130	0·0	—
Dibenzoylmethane	0·2168	19·32	21·5
	0·256	25·4	25·4
Benzoylacetone	0·4224	36·2	58·0
	0·183	17·6	25·1

Action of Magnesium Phenyl Bromide on Dibenzoylmethane.

2·4 Grams of magnesium were treated with 21 grams of bromobenzene in dry ethereal solution, and the product was added to an ethereal solution containing 10 grams of dibenzoylmethane. After keeping overnight, the product was heated for six hours on a steam-bath. After decomposing with ice and with 30 per cent. sulphuric acid, the product, after extracting with ether, was distilled under a pressure of 20 mm. The fraction boiling between 200° and 230° was dissolved in alcohol, and deposited pink crystals of dibenzoylmethane and pale yellow crystals; the latter were separated mechanically and recrystallised from alcohol. They melted at 89°, and gave the following result on analysis:

0·1151 gave 0·3732 CO_2 and 0·0637 H_2O. C = 88·44; H = 6·17.

$C_{21}H_{16}O$ requires C = 88·74; H = 5·63 per cent.

The substance gave no red coloration with ferric chloride, and was insoluble in alkali. It was therefore probably β-benzoyl-αα-diphenylethylene. The yield was exceedingly poor, most of the dibenzoylmethane being recovered unchanged.

In a subsequent experiment, in which an excess of magnesium phenyl bromide (2·4 grams of magnesium and 30 grams of bromobenzene) was added to an ethereal solution of 5 grams of dibenzoylmethane, a very small quantity of yellow crystals, melting at 188°, was obtained; the amount was not sufficient for investigation.

Much of the expense of this investigation has been met by a grant from the Research Fund Committee of the Chemical Society.

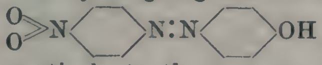
THE UNIVERSITY,
MANCHESTER.

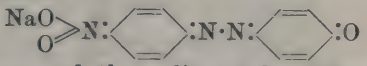
CXXXVIII.—*The Relation between Absorption Spectra and Chemical Constitution. Part XV. The Nitrated Azo-compounds.*

By EDWARD CHARLES CYRIL BALY, WILLIAM BRADSHAW TUCK, and EFFIE GWENDOLINE MARSDEN.

IN a recent paper (this vol., p. 571), we described the results of an investigation of the absorption spectra of a number of aromatic nitro-compounds, and showed that the absorption and colour of these substances is to be explained by the isorropesis between the residual affinity of the nitro-group and that of the phenyl or substituted phenyl residue. We pointed out that the quinonoid theory is entirely unnecessary, and in some cases impossible of acceptance, since it fails in the case of the meta-nitro-derivatives. The quinonoid explanation has received considerable support from a series of investigations by Hewitt and his co-workers on certain nitroazo-compounds. We have examined the same compounds as described by Hewitt, and we find that our results do not support the quinonoid hypothesis, but are very strongly in favour of the explanation put forward in our previous paper.

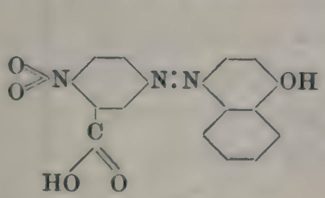
In the first place Hewitt and Mitchell (Trans., 1907, **91**, 1251) deal with the *p*-nitroazophenols, and show that the colour of these compounds changes from yellow to red when they are converted into their alkali metal salts, whilst *p*-nitrobenzene-4-azo-α-naphthol, itself a red substance, gives blue alkali salts. The neutral and alkaline solutions, they say (p. 1255), exhibit absorption of radically different type, except where the presence of inhibiting groups prevents the formation of the diquinonoid structure. They interpret their results by assigning the two structures:



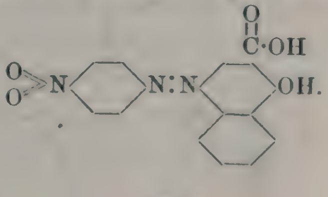


respectively to the parent substance and the sodium salt. Moreover, they say that the parent compound in $N/500$-solution exhibits only general absorption from $\lambda = 500\mu$, whilst the potassium salt in $N/20{,}000$-solution exhibits an absorption band between $\lambda = 532\mu$ and $\lambda = 485\mu$.

A further argument which they bring forward in support of their view that the alkali salts are quinonoid is the relative behaviour of the two isomeric *p*-nitrobenzene-4-azo-α-naphtholcarboxylic acids:

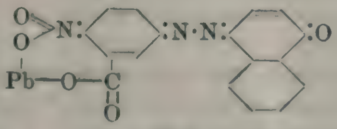


(A.)

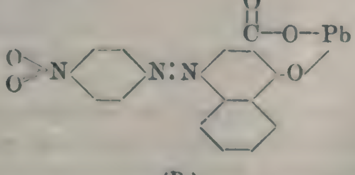


(B.)

Both these compounds give blue solutions in the presence of sodium hydroxide, but compound A gives a blue precipitate with lead acetate, whilst B gives a red precipitate. Hewitt and Mitchell attribute to these precipitates the formulæ:



(A.)



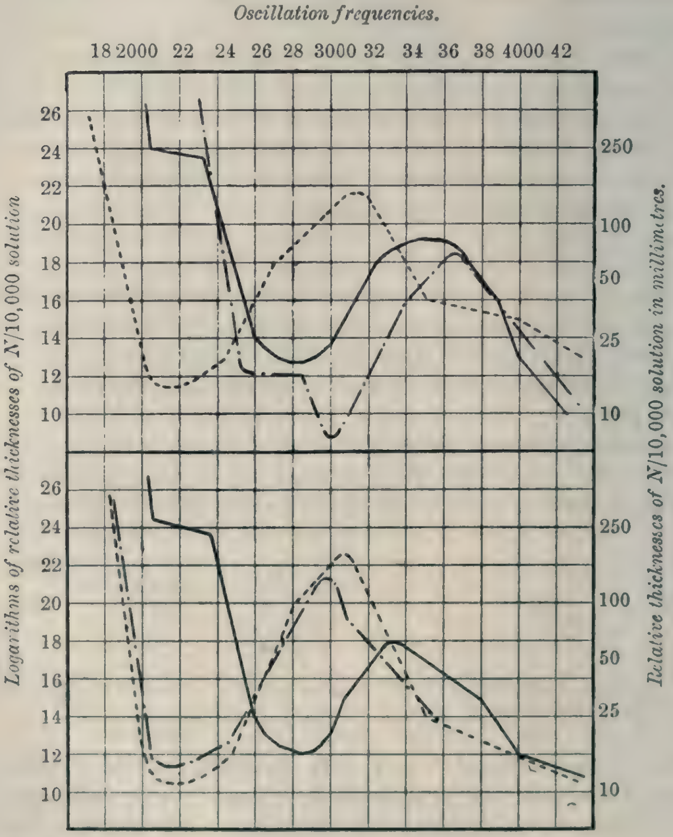
(B.)

As the result of our investigations, we do not agree with Hewitt and Mitchell that there is a radical difference between the absorption of the nitroazophenols and their sodium salts, or between the nitroazonaphthols and their sodium salts. The absorption curves of the two classes of compounds are shown in Figs. 1, 2, and 3, and it may be seen that the absorption with and without alkali is of

FIG. 1.

Upper curves :

Full curve : o-*Nitrobenzeneazophenol in alcohol.*
Dotted curve : o-*Nitrobenzeneazophenol in alcoholic* NaOEt.
Dot and dash curve : p-*Benzoquinoneazine.*



Lower curves :

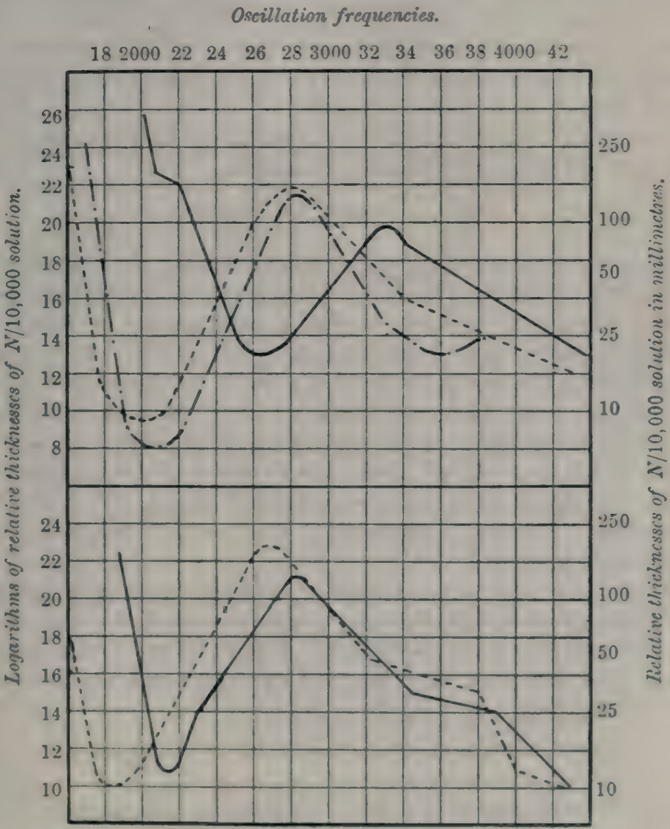
Full curve : m-*Nitrobenzeneazophenol in alcohol.*
Dotted curve : m-*Nitrobenzeneazophenol in alcoholic* NaOEt.
Dot and dash curve : m-*Nitrobenzeneazodimethylaniline in alcohol.*

exactly the same type, the only difference being that there is a shift towards the red on the addition of the alkali. This is exactly similar to the shift observed with the nitrophenols, and is capable of the same explanation, namely, that it is due to the shift which occurs when alkali is added to a solution of phenol itself. If Hewitt and Mitchell had examined *p*-nitrobenzeneazophenol at the same strength as its potassium salt, they would also have found an

FIG. 2.

Upper curves:

Full curve: p-*Nitrobenzeneazophenol in alcohol.*
Dotted curve: p-*Nitrobenzeneazophenol in alcoholic* NaOEt.
Dot and dash curve: p-*Nitrobenzeneazodimethylaniline in alcohol.*



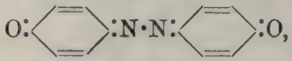
Lower curves:

Full curve: o-*Nitrobenzeneazo-a-naphthol in alcohol.*
Dotted curve: o-*Nitrobenzeneazo-a-naphthol in alcoholic* NaOEt.

absorption band. Exactly the same shift is to be observed with benzeneazophenol as has been previously shown by one of us (Tuck, Trans., 1907, **91**, 450).

We have examined the absorption spectra of the three isomeric nitrobenzeneazophenetoles, and find them identical with those of the corresponding nitrobenzeneazophenols. The absorption spectra of the nitrobenzeneazodimethylanilines were also investigated; only the *m*- and *p*-isomerides were prepared, and it was found that their absorption is very similar to that of the corresponding sodium nitrobenzeneazophenoxides (see Figs. 1 and 2). Since it is, of course, impossible for the former compounds to be quinonoid, this similarity argues strongly against the quinonoid structure of the sodium salts of the nitroazophenols.

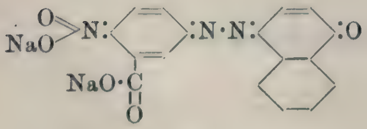
In order to obtain conclusive evidence, we have examined the absorption spectrum of *p*-benzoquinoneazine,



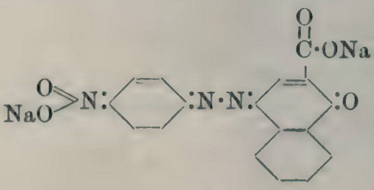
which contains the diquinonoid linking exactly as is claimed by Hewitt and Mitchell for the sodium salt of *p*-nitrobenzeneazophenol. The curve is shown in Fig. 1, and, as can be seen, bears no resemblance to any of the nitroazophenol curves. It is evident therefore that the latter compounds cannot be quinonoid.

In reference to *p*-benzoquinoneazine, a very striking resemblance exists between its absorption and those of the *o*-hydroxyazo-compounds which one of us, from observations of their absorption spectra, concluded were quinonehydrazones (Tuck, *loc. cit.*). The result given by benzoquinoneazine is additional evidence in favour of this conclusion.

Turning to the two isomeric *p*-nitrobenzeneazo-α-naphtholcarboxylic acids mentioned above, it appears to us that the argument of Hewitt and Mitchell is fallacious. Both acids are blue in alkaline solution, and therefore, according to their view, both are quinonoid, that is, they have the formulæ:



(A.)



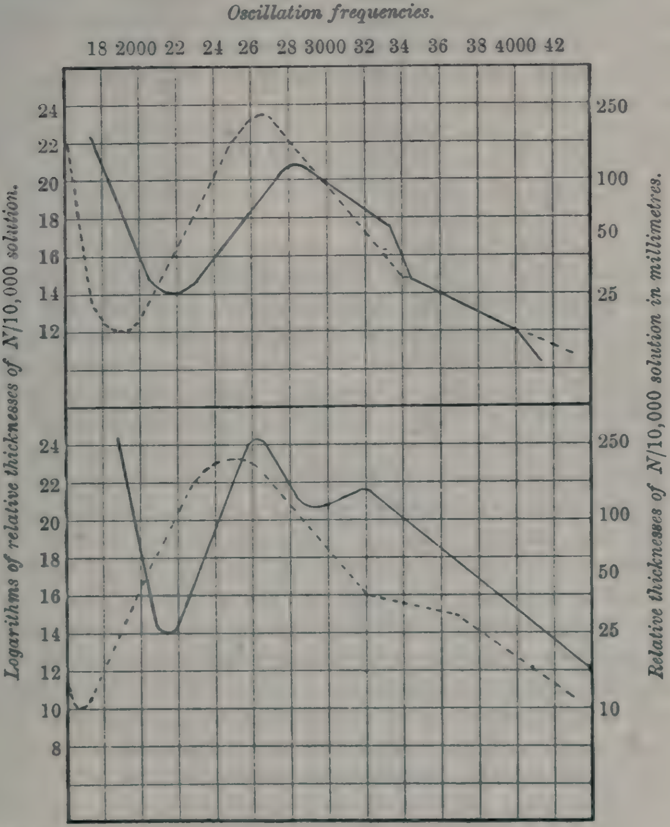
(B.)

Now, in A it is true that there are two neighbouring ONa groups which may give a lake, but this is not the case in B, for the two ONa groups are at opposite ends of the molecule. It is therefore impossible for Hewitt and Mitchell's lake formation to take place

FIG. 3.

Upper curves:

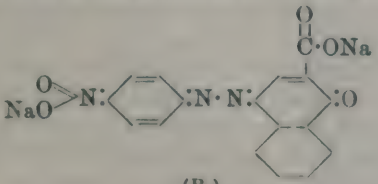
Full curve: m-*Nitrobenzeneazo-α-naphthol in alcohol.*
Dotted curve: m-*Nitrobenzeneazo-α-naphthol in alcoholic* NaOEt.



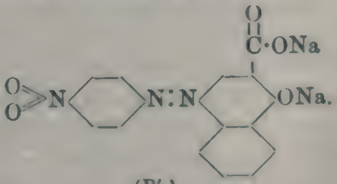
Lower curves:

Full curve: p-*Nitrobenzeneazo-α-naphthol in alcohol.*
Dotted curve: p-*Nitrobenzeneazo-α-naphthol in alcoholic* NaOEt.

in B unless the Na attached to the NO_2 group were tautomeric. If it were labile, then the two forms B and B′ would be in equilibrium:



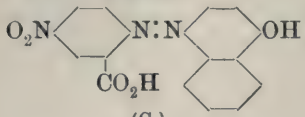
(B.)



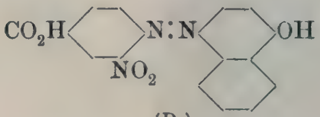
(B′.)

But the whole essence of the argument depends on there not being any such equilibrium in existence, for if an equilibrium did exist it would be impossible to attribute a definite reaction, such as lake formation, to one phase and one phase only. It appears therefore to us that Hewitt and Mitchell's deduction of the quinonoid structure from the lake formation is unsound.

Now, we have prepared and investigated the properties of the two isomeric acids:


(C.)

and


(D.)

and we find that C, which is blue in alkaline solution, also gives a blue precipitate with lead acetate, whilst D, which is purple in alkaline solution, gives a purple precipitate with barium chloride. As in neither case are there two adjacent hydroxyl groups, it follows that the formation of insoluble "lakes" cannot in any way be taken as evidence of there being two such adjacent groups.

We have further investigated the reactions of the above two acids (C and D) and also of Hewitt and Mitchell's acid (B), and we find that various coloured precipitates can be obtained with the greatest ease according to the strength of the solution. The explanation lies in the fact that the sodium salts of the three acids form colloidal solutions and may be precipitated at once by the addition of *any metallic salt*. For example, if to a strong aqueous solution of the sodium salt of Hewitt and Mitchell's acid (B) a few drops of an aqueous solution of sodium chloride be added, the sodium salt is thrown down as an insoluble *blue* precipitate. If, on the other hand, a dilute solution of the sodium salt be used, the addition of the sodium chloride solution turns it red, and in a few moments the acid itself is thrown down as a *red* precipitate. Exactly the same is true in the case of the two isomeric acids A and B above. It appears therefore that no evidence whatever as regards structure can be obtained from the behaviour of these acids with lead acetate. The evidence obtained from the absorption spectra is overwhelmingly against the quinonoid configuration of the nitrobenzeneazophenols and α-naphthols, and we therefore attribute the same explanation as was put forward in our previous paper, namely, that the absorption is due to the association of the residual affinities of the nitrophenyl, azo-, and phenol or naphthol groupings, and that the shift of the absorption band on the addition of alkali is due to the same cause as the shift in the absorption of phenol itself when alkali is added. It may be seen from the figures that in the case of the nitrobenzeneazophenols the shifts produced by the addition of alkali to the ortho-, meta-, and para-isomerides are 670, 700, and 600 units respectively. In the case of the corresponding naphthols, the shifts are 280, 300, and 470 units respectively. The shift therefore given by the meta-isomeride is of the same order as those given by the ortho- and para-isomerides.

EXPERIMENTAL.

o-*Nitrobenzeneazophenetole*.—This was prepared by boiling *o*-nitrobenzeneazophenol in alcoholic solution with ethyl bromide and sodium ethoxide for about one hour. The ether crystallises from dilute alcohol in small, flat, bronze needles, melting at 88°:

0·1195 gave 16·0 c.c. N_2 (moist) at 19° and 764·2 mm. N = 15·52.

$C_{14}H_{13}O_3N_3$ requires N = 15·5 per cent.

m-*Nitrobenzeneazophenetole*.—Prepared in the same way as the ortho-isomeride. Crystallises from alcohol in flat, yellow needles, melting at 96°:

0·1194 gave 16·1 c.c. N_2 (moist) at 18° and 761·2 mm. N = 15·64.

$C_{14}H_{13}O_3N_3$ requires N = 15·5 per cent.

p-*Nitrobenzeneazophenetole*.—Prepared in the same way as the two preceding compounds. Crystallises from alcohol in very small, dark yellow needles, melting at 155°:

0·1153 gave 15·4 c.c. N_2 (moist) at 16° and 747·2 mm. N = 15·63.

$C_{14}H_{13}O_3N_3$ requires N = 15·5 per cent.

o-*Nitro*-o-*carboxybenzene*-4-*azo*-α-*naphthol*.—This was prepared by diazotising 3-nitro-4-aminobenzoic acid with amyl nitrite, and pouring the resulting solution into the α-naphthol dissolved in sodium hydroxide. The sodium salt was decomposed by dilute sulphuric acid, and steam was passed through the mixture for half an hour. The azo-compound was recrystallised from nitrobenzene. It forms red, microscopic needles, which melt and decompose at 313°:

0·1209 gave 13·2 c.c. N_2 (moist) at 24° and 758 mm. N = 12·25.

$C_{17}H_{11}O_5N_3$ requires N = 12·46 per cent.

The 3-nitro-4-aminobenzoic acid was prepared from aceto-*p*-toluidide. This was nitrated by slowly adding it to nitric acid (D 1·45). The nitro-compound was then oxidised by suspension in water through which a current of steam was led, while finely powdered potassium permanganate (2 mols.) was added in small quantities exactly as described by Hewitt and Mitchell. The resulting nitro-acetylaminobenzoic acid was hydrolysed in the following way. To a boiling concentrated solution of the acid in alcohol, an equal volume of concentrated aqueous hydrochloric acid was added, and the mixture boiled for about one minute. The nitroaminobenzoic acid then began to crystallise in well-formed needles, and, on cooling and adding water, the acid was obtained in a very pure state. The yield is almost quantitative.

p-*Nitro*-o-*carboxybenzene-4-azo-α-naphthol*.—This was prepared by diazotising 5-nitro-2-aminobenzoic acid, and pouring into a solution of α-naphthol. The compound was recrystallised from nitrobenzene. It forms chocolate, microscopic needles, which melt and decompose at 303°:

0·1350 gave 14·4 c.c. N_2 (moist) at 22° and 766·2 mm. N = 12·23.
$C_{17}H_{11}O_5N_3$ requires N = 12·46 per cent.

The 5-nitro-2-aminobenzoic acid was prepared in two ways. The first quantity was obtained from aceto-*o*-toluidide by nitration and subsequent oxidation by potassium permanganate to 5-nitro-2-acetylaminobenzoic acid. The acetylamino-compound was hydrolysed in the same way as described above. The yield of the acetylamino-compound was, however, very poor, and a second quantity was prepared by direct nitration of acetylanthranilic acid; 75 grams were slowly added to 150 grams of nitric acid (D 1·49), and then kept for two hours. This period was found to be absolutely necessary. The mixture was then poured on ice; the yield of the nitro-compound is about 85 per cent.

We wish, in conclusion, to express our thanks to the Chemical Society for a grant in aid of this work.

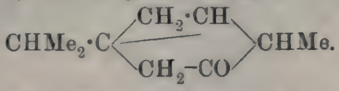
Spectroscopic Laboratory,
University of London,
University College.

CXXXIX.—*A Contribution to the Study of Tanacetone (β-Thujone) and some of its Derivatives.*

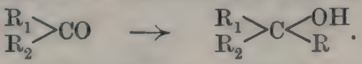
By David Thomson (late 1851 Exhibition Research Scholar).

The present paper contains a brief summary of the experimental work described in the author's dissertation (Göttingen, 1909). The work was carried out between October, 1907, and March, 1909, in Göttingen, under the supervision of Geh. Reg. Rat. Prof. Dr. O. Wallach, to whom the author desires to express his grateful thanks. The experiments had a twofold object in view: first, the chemical and optical study of tanacetone (β-thujone) and some of its derivatives; secondly, the preparation of a series of active compounds, the study of which seemed likely to throw some light on the problem of the relationship between optical activity and chemical constitution. In this paper only the experimental data are given. A discussion of the optical data bearing on the question of optical activity and chemical constitution is reserved for a subsequent paper, when some experiments, at present in progress, on the condensation products of active 1-methyl*cyclo*hexan-3-one have been completed.

Application of the Grignard Reaction to Tanacetone,



The application of the Grignard reagent to a ketone yields, as is well known, a tertiary alcohol according to the equation:

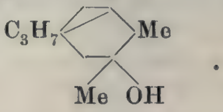


$$\begin{matrix}R_1\\R_2\end{matrix}\!\!>CO \longrightarrow \begin{matrix}R_1\\R_2\end{matrix}\!\!>C<\!\!\begin{matrix}OH\\R\end{matrix}.$$

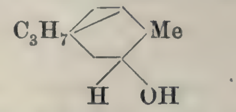
When R, R_1, R_2 are all different, as with tanacetone, the carbon atom to which these groups are attached becomes asymmetric in the process. Since tanacetone is optically active, two tertiary alcohols must be expected with the rotations $+A+B$ and $+A-B$ respectively, where A denotes the rotation of tanacetone and $\pm B$ that of the new asymmetric carbon atom. These two alcohols will not, however, be optical antipodes, and hence may be capable of mechanical separation. This proved to be the case. Tanacetone treated with magnesium methyl iodide yielded two tertiary alcohols, one liquid and one solid, which could be easily separated by cooling in a freezing mixture. The liquid alcohol boils at 202—205°, and has the specific rotation $+35{\cdot}8°$ ($p=5{\cdot}226$ in ether); the solid alcohol melts at 84°, $[\alpha]_D$ $-30{\cdot}5°$ ($p=4{\cdot}058$ in ether). The observation of rotatory power for the liquid alcohol is probably low, as it is unlikely that a complete separation of the solid alcohol was effected by the freezing-out process.

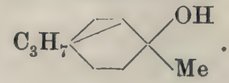
As the separation of the two isomeric homothujyl alcohols had proved so easy, the method was tried with the higher homologues, namely, the ethyl-, propyl-, and *iso*propyl-thujyl alcohols, but without success. The product of the Grignard reaction was in each case an oil which could not be separated into its isomeric constituents. Some *iso*thujone, with which Prof. Wallach kindly furnished the author, on treatment with magnesium methyl iodide, gave a similar result. Separation of the oily reaction product into its two isomeric constituents proved an insuperable difficulty. In all these cases the absence of unattacked tanacetone was proved by treatment with semicarbazide solution.

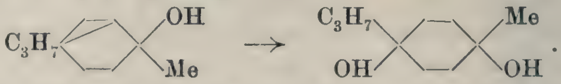
Stability of the cyclo*Propane Ring in the two Homothujyl Alcohols,*



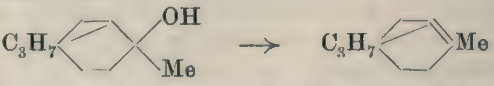
As this question has already been discussed by Wallach (*Annalen*, 1908, **360**, 86), the results of the experiments need only be mentioned here. Both alcohols, like thujyl alcohol,



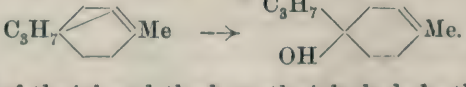
are not affected by long shaking with 5 per cent. sulphuric acid. Very different is the behaviour of the similarly constituted sabinene hydrate,  By the same treatment it is converted into *p*-menthan-1 : 4-diol :



Wallach (*loc. cit.*) shows that the formation of this dihydric menthane does not take place directly, but indirectly, from Δ^5-*p*-menthen-4-ol ; and he finds in this intermediate product the clue to the difference in stability of the *cyclo*propane ring in sabinene hydrate and in thujyl and homothujyl alcohol. He assumes that the first action of the dilute sulphuric acid is to eliminate water, thus :



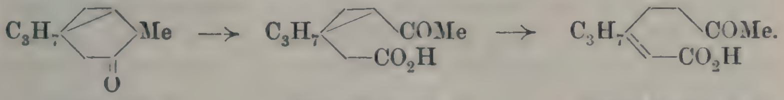
a reaction rendered all the easier by the mobility of the hydrogen atom attached to the tertiary carbon atom. The formation of the quaternary carbon atom, however, so weakens the stability of the *cyclo*propane ring that combination with water takes place at once, thus :



In the case of thujyl and the homothujyl alcohols, the formation of a double bond in immediate juxtaposition to the *cyclo*propane ring is hindered by the position of the hydroxyl group ; hence the greater stability of these compounds. This explanation suffices to explain the behaviour of a great many terpenes towards dilute sulphuric acid, and we shall see presently that it is capable of application to the acids derived from tanacetone by oxidation.

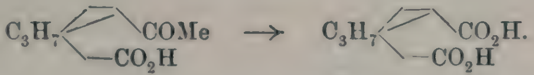
Oxidation Products of Tanacetone (β-Thujone).

Wallach (*Annalen*, 1893, **272**, 113; 1904, **336**, 266) has shown that when tanacetone is oxidised with a neutral solution of 5 per cent. permanganate, a mixture of two ketonic acids, distinguished as α- and β-thujaketonic acid, is produced. The α-acid is saturated and optically active; the β-acid is unsaturated and optically inactive. The formation of these acids from tanacetone is explained thus:

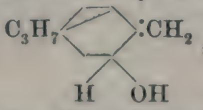


Tanacetone. α-Thujaketonic acid. β-Thujaketonic acid.

The α-acid may be readily converted into the β-acid by distillation (Wallach, *Annalen*, 1893, **275**, 166). Both the α- and the β-acids, when further oxidised with sodium hypobromite, yield the corresponding dicarboxylic acids (Semmler, *Ber.*, 1892, **25**, 3348), for example:



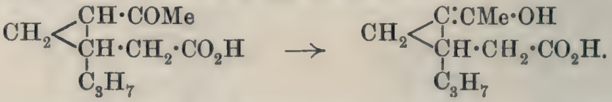
α-Thujadicarboxylic acid.

α-Thujadicarboxylic acid—called by Semmler α-tanacetonedicarboxylic acid—may also be produced by the direct oxidation of sabinol, , with permanganate (Fromm, *Ber.*, 1898, **31**, 2030). Several hundred grams of both α-thujaketonic and α-thujadicarboxylic acid were prepared.

The method adopted in the preparation of α-thujaketonic acid was, with but slight modification, that of Wallach (*loc. cit.*). Curiously enough, and in apparent contradiction to the result cited, it was found that whether the oxidation was carried out with warm or cold permanganate solution only one acid, namely, the α-acid, was produced. As the two ketonic acids are sharply distinguished in crystalline form—the α-acid crystallising in plates, the β-acid in needles—and in solubility, and as a careful watch was kept for any appearance of β-acid, its presence could scarcely have escaped detection. Whether this result is to be ascribed to some difference in the tanacetone used or to the omission of the distillation in steam of the product of oxidation—which was the essential variation of Wallach's method adopted—is not yet quite clear.

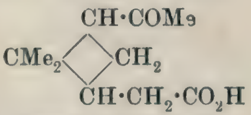
Stability of the cyclo*Propane Ring in α-Thujaketonic and α-Thujadicarboxylic Acids.*

Very remarkable is the difference in stability of the *cyclo*propane ring in α-thujaketonic and α-thujadicarboxylic acid. The ketonic acid is rapidly decomposed by boiling 20 per cent. hydrochloric acid, with formation of an inactive unsaturated hydrocarbon, which has the characteristic odour of dihydro-ψ-cumene, and boils at 160—165° (dihydro-ψ-cumene boils at 160°). The dicarboxylic acid is not affected in rotation and melting point by two hours' vigorous boiling with 20 per cent. hydrochloric acid, and shows a like stability towards boiling 10 per cent. sodium hydroxide. If one accepts the above explanation given by Wallach for the difference in stability of sabinene hydrate and homothujyl alcohol, the difference in stability of these two acids presents no difficulty. The first effect of the boiling hydrochloric on the ketonic acid is, presumably, to convert it into its enolic form:

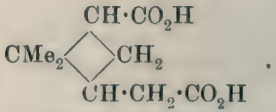


$$CH_2<\begin{matrix}CH\cdot COMe\\ |\\ CH\cdot CH_2\cdot CO_2H\\ |\\ C_3H_7\end{matrix} \longrightarrow CH_2<\begin{matrix}C{:}CMe\cdot OH\\ |\\ CH\cdot CH_2\cdot CO_2H.\\ |\\ C_3H_7\end{matrix}$$

The formation of the quaternary carbon atom, however, so diminishes the stability of the *cyclo*propane ring that decomposition at once takes place. With the dicarboxylic acid, on the other hand, such enolisation is impossible; hence its greater stability. Similar results were obtained by von Baeyer (*Ber.*, 1896, **29**, 326) with pinonic and pinic acids:



Pinonic acid (unstable).



Pinic acid (stable).

Esterification of α-Thujadicarboxylic Acid.

The great stability of α-thujadicarboxylic acid towards hydrochloric acid having been proved, the esterification of this acid in the ordinary way by passing hydrogen chloride into the alcoholic solution of the acid was successfully attempted. *Dimethyl*, *diethyl*, *di*-n-*propyl*, *di*iso*butyl*, and *di*iso*amyl* esters were so prepared. The dimethyl and diethyl esters were easily obtained in a pure state; the esters of the other three alcohols were, as the boiling points and the results of analysis indicate, never quite free from traces of impurity, most likely acid esters. An attempt to prepare a dibenzyl ester gave a compound which the results of analysis indicate to be a *monobenzyl* ester.

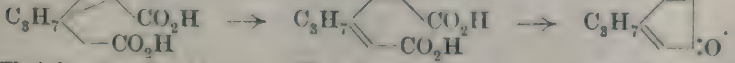
All these esters are clear, odourless, more or less viscous liquids. The absence of odour is rather remarkable. With the exception of the monobenzyl ester, which is pale yellow, they are quite colourless. They are very stable compounds, and do not give acid amides when shaken with a strong solution of ammonia. The methyl and ethyl esters were saponified, and the acid recovered. Melting point and rotatory power were unchanged. Hence there was no racemisation during the process of esterification.

The constants for these esters are given in the subjoined table. Details will be found in the experimental part. The boiling points were taken under a pressure of 10—14 mm.; the temperature at which the densities were taken also varied from 15° to 20°; hence the figures are not exactly comparable:

	B. p. (10—14 mm.)	$d_{(15-20°)}$.	$[\alpha]_D$.
Dimethyl ester	126—127°	1·0535	+142·5°
Diethyl ester................	138—140	1·019	114·1
Di-*n*-propyl ester	157—160	0·9969	84·7
Di*iso*butyl ester	174—177	0·9908	77·6
Di*iso*amyl ester	187—190	0·9924	73·5
Monobenzyl ester (?)......	215—220	—	34·7

Decomposition Products of the Sodio-derivatives of the Dimethyl (and Diethyl) Esters of α-Thujadicarboxylic Acid.

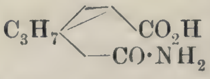
The dimethyl and diethyl esters of α-thujadicarboxylic acid in solution in dry ether react slowly with metallic sodium, giving a sodio-derivative. An attempt to replace the sodium atom by an ethyl group failed, owing to the instability of the compound formed. On warming the sodio-derivative of the dimethyl (or diethyl) ester with water, and distilling the reaction mixture in a current of steam, an excellent yield of tanacetophorone was obtained. The tanacetophorone prepared in this way is much purer than that obtained by the distillation of thujadicarboxylic acid over soda-lime. The formation of tanacetophorone by the latter process depends, according to Semmler (*Ber.*, 1892, **25**, 3350), on the conversion of α-thujadicarboxylic acid into β-thujadicarboxylic acid, which then loses carbon dioxide and undergoes intramolecular condensation, thus:



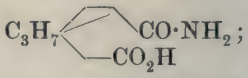
α-Thujadicarboxylic acid. β-Thujadicarboxylic acid. Tanacetophorone.

If this explanation held in the present instance, then β-thujadicarboxylic acid was to be expected among the residues in the distilling flask. Careful examination did reveal an inactive acid, the melting point of which was identical with that of β-thujadicarboxylic acid, namely, 116—117°. Along with it, and in slightly greater quantity, was another inactive acid, which melted at 150—151°, or nine degrees higher than α-thujadicarboxylic acid. The nature of this acid has not yet been determined with certainty. Analysis proves it to be isomeric with the α- and β-dicarboxylic acids. It is probably racemic α-thujadicarboxylic acid.

Monoamide of α-Thujadicarboxylic Acid.—The anhydride of α-thujadicarboxylic acid reacts readily with ammonia, aniline, or piperidine. The additive product with piperidine is a liquid, with aniline, a glass. With ammonia, after some difficulty, a well-defined crystalline *monoamide* was obtained. It melted at 149—150°, and had $[\alpha]_D^{15}$ $+54{\cdot}5°$ ($p = 3{\cdot}777$ in methyl alcohol). Its formula must be either



or



which is the true one, however, has not yet been determined. The *ammonium* salt of the monoamide was also prepared. Its specific rotation is $+9{\cdot}2°$ ($p = 4{\cdot}694$ in methyl alcohol).

EXPERIMENTAL.

All rotations were measured with a Schmidt and Haensch half-shadow polarimeter. The instrument was not equipped with a thermostat, and hence it was impossible to measure rotations at a definite temperature. Densities were determined with a Mohr-Westphal balance, and therefore refer to water at 15°.

The tanacetone used in the following experiments was furnished by Schimmel & Co. It was purified before use by distillation under atmospheric pressure; the fraction boiling at 200—207° was then rectified once or twice under diminished pressure. The final product was a colourless oil of pleasant odour, with the following constants:

b. p. 81—82°/11 mm.; $d_{12/15} = 0{\cdot}924$; $[\alpha]_D^{12}$ $+67{\cdot}4°$.

As a specimen of crude tanacetone, which had been kept for a long time in the laboratory, showed a specific rotation of about +30°, it was deemed advisable to test the keeping qualities of the tanacetone used. A portion purified as above described was accordingly set aside, and its rotation examined from time to time. Its initial rotation was $\alpha_D^{12} + 62{\cdot}3°$, and after fifty-one weeks, $\alpha_D^{17} + 60{\cdot}1°$; tanacetone therefore racemises with extreme slowness.

Application of Grignard Reagent to Tanacetone and iso*Thujone.*

To ensure an excess of the Grignard reagent, 2 molecular proportions of magnesium and 2 of alkyl iodide were invariably used to one of the ketone. The reaction mixture was either poured on ice, acidified with acetic acid, and then extracted with ether, or, after pouring on ice, the whole was distilled in a current of steam, and the tertiary alcohol formed was extracted from the distillate by means of ether. The product of the treatment of tanacetone with magnesium methyl iodide was a yellow oil. This was distilled under atmospheric pressure, and the distillate well cooled in a freezing mixture. Partial solidification at once took place. The solid crystallised from methyl alcohol in white needles, melting at 84°:

0·2295 gave 0·6600 CO_2 and 0·2482 H_2O. $C = 78{\cdot}42$; $H = 12{\cdot}13$.

$C_{11}H_{20}O$ requires $C = 78{\cdot}49$; $H = 12{\cdot}01$ per cent.

Rotatory power:

$p = 4{\cdot}058$ in ether; $d_{15{\cdot}5} = 0{\cdot}728$; $l = 2{\cdot}2$ dcm.; $\alpha_D - 1{\cdot}93°$, $[\alpha]_D^{15{\cdot}5} - 30{\cdot}5°$.

$p = 4{\cdot}191$ in methyl alcohol; $d_{12} = 0{\cdot}8055$; $l = 2{\cdot}2$ dcm.; $\alpha_D - 1{\cdot}93°$; $[\alpha]_D^{12} - 26{\cdot}0°$.

The process of cooling and filtering was repeated until no more solid separated, and the remaining oil was distilled. The main fraction boiled at 204°. To make certain of the absence of unattacked tanacetone, the oil was treated several times with semicarbazide solution. Not a trace of semicarbazone was obtained after long keeping. Hence the absence of tanacetone is proved. The results of analysis were in agreement with theory.

Rotatory power:

$p = 5{\cdot}226$ in ether; $d_{14} = 0{\cdot}731$; $l = 2{\cdot}2$ dcm.; $\alpha_D^{14} + 3{\cdot}016°$; $[\alpha]_D^{14} + 35{\cdot}9°$.

$p = 5{\cdot}077$ in methyl alcohol; $d_{13} = 0{\cdot}8050$; $l = 2{\cdot}2$ dcm.; $\alpha_D^{13} + 3{\cdot}00°$; $[\alpha]_D^{13} + 33{\cdot}4°$.

Curiously enough, neither the solid nor the liquid alcohol gives a urethane when treated with phenylcarbimide.

Stability of the cyclo*Propane Ring in the Homothujyl Alcohols.*

One gram of solid homothujyl alcohol (m. p. 84°) was suspended in 500 c.c. of 5 per cent. sulphuric acid, and mechanically shaken daily for three weeks. The reaction mixture was then carefully neutralised with sodium hydroxide, and distilled in a current of steam for ten minutes in order to remove unattacked alcohol. The liquid in the distilling flask was then cooled and thoroughly extracted with ethyl acetate. After evaporation of the solvent, mere traces of an additive product were found.

Five grams of the liquid homothujyl alcohol, when treated in the same way with 1 litre of 5 per cent. sulphuric acid, gave a similar result.

Preparation of α-Thujaketonic Acid from Tanacetone.

Seventy-five grams of crude tanacetone (α_D +64°) were treated with the calculated amount (two atomic proportions of oxygen) of 5 per cent. permanganate solution, and the mixture was shaken mechanically until the permanganate was decolorised (two to three hours). The manganese oxide was then filtered off, and the filtrate evaporated on the water-bath until a skin began to form on the surface. If, before evaporating, oily drops (unattacked tanacetone or *l*-fenchone) were seen floating on the surface of the liquid, these were removed by means of a separating funnel. In order to prevent any harmful action of the alkali during the process of evaporation, small quantities of a solution of sulphurous acid were added from time to time, care being taken never to make the liquid acid in reaction. As soon as a skin began to form on the surface of the liquid, it was filtered, cooled, and acidified with dilute sulphuric acid. The α-thujaketonic acid usually separated at once in solid form. On crystallisation from boiling water, it melted at 75—76°; 75 grams of tanacetone gave 45 to 50 grams of α-thujaketonic acid.

Rotatory Power of α-Thujaketonic Acid (m. p. 75—76°).

Solvent.	*p.*	*d.*	*l.*	α_D.	$[\alpha]_D$.
Ether	6·945	0·742 (14°)	2·2 dcm.	+22·00 (14°)	+194·0°
Glacial acetic acid..	4·6163	1·0524 (19)	1 ,,	10·886 (19)	224·1
Methyl alcohol......	5·5649	0·8064 (19)	1 ,,	9·64 (19)	214·8
Chloroform	5·132	1·458 (16)	1 ,,	18·313 (16)	244·8
Water	0·6754	1·002 (18)	2·2 ,,	3·633 (18)	244·0

As the rotations of the oxime and semicarbazone of α-thujaketonic acid have never hitherto been published, these compounds, together with its ammonium salt, were prepared and their rotations examined.

Rotatory Power of Semicarbazone of α-Thujaketonic Acid
(m. p. 183—184°).

$p = 2{\cdot}290$ in glac. acetic acid; $d_{16} = 1{\cdot}0605$; $l = 2{\cdot}2$ dcm.; α_D^{16} $+12{\cdot}17°$; $[\alpha]_D^{16}$ $+227{\cdot}8°$.

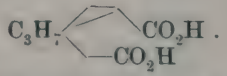
Oxime of α-Thujaketonic Acid.—This compound was prepared in two different ways, namely, in alkaline and in neutral solution. The products obtained after recrystallisation from methyl alcohol differed both in melting point and in rotatory power. The oxime prepared in alkaline solution according to Lazell's method (*Diss.,* Göttingen, 1896, p. 26) melted at 169—170°, in good agreement with his result (169°), and had $[\alpha]_D$ −5·00° in methyl alcohol ($p = 3{\cdot}933$).

The oxime prepared in neutral solution melted at 174—175°, and showed the following rotation values: $p = 4{\cdot}473$ in methyl alcohol—no measurable rotation; $p = 1{\cdot}7008$ in glacial acetic acid; $d_{14} = 1{\cdot}058$; $l = 1$-dcm.; α_D +0·10°; $[\alpha]_D$ +5·56°. In dilute sodium hydroxide solution the rotation was strongly negative. It was at first thought that these two oximes were stereoisomerides. Careful comparison has, however, since proved that this is not the case. By repeated crystallisation from methyl alcohol, the oxime of lower melting point is converted into the other, and a mixture of the two then melts unchanged at 174—175°.

Rotatory Power of the Ammonium Salt of α-Thujaketonic Acid.

$p = 0{\cdot}881$ in water; $d_{19} = 1{\cdot}007$; $l = 2{\cdot}2$ dcm.; α_D^{19} +3·333°; $[\alpha]_D^{19}$ +170°.

α-Thujadicarboxylic Acid,



$C_3H_7{<}\begin{matrix}CO_2H\\CO_2H\end{matrix}$.

The α-thujadicarboxylic acid used was prepared by the methods of both Semmler and Fromm (*loc. cit.*). The larger portion was, however, prepared by Semmler's method from α-thujaketonic acid. It melted at 141—142°.

Rotatory power:

Solvent.	*p.*	*d.*	*l.*	α_D.	$[\alpha]_D$.
Ether	4·991	0·734 (15°)	2·2 dcm.	+8·47 (15°)	+105·1°
Glacial acetic acid ...	4·9177	1·0586 (18)	1 ,,	6·933 (18)	133·2
Chloroform	2·8726	1·480 (15)	1 ,,	7·29 (15)	171·5
Methyl alcohol	4·7043	0·810 (16)	1 ,,	3·96 (16)	104·0
Water	0·7323	1·003 (18)	2·2 ,,	2·183 (18)	135·1

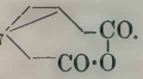
Rotatory Power of Ammonium Hydrogen Salt of α-Thujadicarboxylic Acid.

$p = 0{\cdot}793$ in water; $d_{17} = 1{\cdot}005$; $l = 2{\cdot}2$ dcm.; α_D^{17} +0·266°; $[\alpha]_D^{17}$ +15·2°.

Rotatory Power of Normal Ammonium Salt of α-Thujadicarboxylic Acid.

$p = 3{\cdot}805$ in water; $d_{18} = 1{\cdot}0105$; $l = 2{\cdot}2$ dcm.; α_D^{18} −0·453°; $[\alpha]_D^{18}$ −5·3°.
$p = 1{\cdot}90$ in water; $d = 1{\cdot}00$; $l = 2{\cdot}2$ dcm.; α_D −0·30°; $[\alpha]_D$ −7·1°.

Anhydride of α-Thujadicarboxylic Acid, C_3H_7



This compound was first prepared by Semmler (*Ber.*, 1892, **25**, 3349). Its rotation has not previously been published.

Rotatory power:

$p = 4{\cdot}069$ in ether; $d_{17} = 0{\cdot}730$; $l = 1$ dcm.; α_D^{17} $+0{\cdot}30°$; $[\alpha]_D^{17}$ $+10{\cdot}1°$.
$p = 2{\cdot}642$ in chloroform; $d_{13} = 1{\cdot}481$; $l = 1$ dcm.; α_D^{13} $+0{\cdot}33°$; $[\alpha]_D^{13}$ $+8{\cdot}43°$.

Heating with dilute hydrochloric acid converts the anhydride readily into the original acid.

Preparation of the Monoamide of α-Thujadicarboxylic Acid and its Ammonium Salt.

Five grams of the pure anhydride of α-thujadicarboxylic acid (m. p. 56°), prepared as described by Semmler (*loc. cit.*), were dissolved in warm absolute alcohol, and the well-cooled solution saturated with dry ammonia gas. On keeping, a white solid slowly separated. This was dissolved in the least possible amount of water, and the solution rendered just acid with hydrochloric acid. Either at once or on keeping, fine white crystals separated, which were sparingly soluble in water, ether, or chloroform, readily so in alkalis. They were purified by redissolving in the least possible amount of dilute ammonia solution, and precipitating with hydrochloric acid. The substance melted at 149—150°, or eight degrees higher than α-thujadicarboxylic acid:

0·1796 gave 0·3844 CO_2 and 0·1318 H_2O. C = 58·37; H = 8·209.
$C_9H_{15}O_3N$ requires C = 58·34; H = 8·167 per cent.

Rotatory power in methyl alcohol:

$p = 3{\cdot}777$; $d_{15} = 0{\cdot}8084$; $l = 1$ dcm.; α_D^{15} $+1{\cdot}666°$; $[\alpha]_D^{15}$ $+54{\cdot}5°$.

Three hours later the rotatory power was unchanged.

The white solid which separated from the ammonia-alcoholic solution of the anhydride was recrystallised from absolute alcohol and analysed. It proved to be the *ammonium* salt of the monoamide:

0·1813 gave 0·3637 CO_2 and 0·1473 H_2O. C = 54·71; H = 9·088.
$C_9H_{18}O_3N_2$ requires C = 53·42; H = 8·973 per cent.

The high result for carbon is satisfactorily accounted for by the presence of traces of the monoamide, doubtless formed by hydrolysis during the process of crystallisation.

Rotatory power:

$p=1\cdot713$ in water; $d_{17}=1\cdot006$; $l=2\cdot2$ dcm.; α_D^{17} $-0\cdot666°$; $[\alpha]_D^{17}$ $-17\cdot6°$.

$p=4\cdot694$ in methyl alcohol; $d_{18}=0\cdot808$; $l=1$ dcm.; α_D^{18} $+0\cdot35°$; $[\alpha]_D^{18}$ $+9\cdot2°$.

Stability of the cyclo*Propane Ring in α-Thujaketonic Acid.*

Ten grams of α-thujaketonic acid were dissolved in 1000 c.c. of 20 per cent. hydrochloric acid, and boiled for two hours. Steam was then passed into the mixture for fifteen minutes, and an oil distilled over which proved to be an unsaturated hydrocarbon identical in odour with dihydro-ψ-cumene. When rectified over sodium, it boiled at 160—165° (dihydro-ψ-cumene boils at 160°). An attempt to characterise it more nearly by preparation of the crystalline trinitrodihydro-ψ-cumene failed. From the residues in the distilling flask, a large quantity of an inactive acid oil was obtained. All attempts to crystallise this oil failed.

Stability of the cyclo*Propane Ring in α-Thujadicarboxylic Acid.*

One gram of the acid was boiled for two hours with 20 per cent. hydrochloric acid, and the substance then recovered by evaporation on the water-bath. It melted at 141—142° (unchanged), and had $[\alpha]_D$ ($p=2\cdot703$ in ether) $+109°$ [the pure substance has $[\alpha]_D$ ($p=4\cdot991$ in ether) $+105°$].

One gram of the acid, boiled for one and a-half hours with 10 per cent. sodium hydroxide solution, gave a similar result.

Esterification of α-Thujadicarboxylic Acid.

The esterification was carried out in the usual way by saturating the alcoholic solution of the acid with hydrogen chloride.

Dimethyl Ester, $C_7H_{12}(CO_2Me)_2$.

B. p. 126—127°/13 mm.; under the ordinary pressure 244—247°; $d_{20}=1\cdot0535$; $n_D=1\cdot4506$. When boiled for two hours with aniline under reflux, it does not give an anilide. It reacts with metallic sodium in ethereal solution, giving a sodio-derivative:

0·2153 gave 0·4853 CO_2 and 0·1684 H_2O. C = 61·47; H = 8·756.

$C_{11}H_{18}O_4$ requires C = 61·65; H = 8·472 per cent.

Rotatory power:

$d_{18}=1\cdot054$; $l=1$ dcm.; α_D^{18} $+150\cdot18°$; $[\alpha]_D^{18}$ $+142\cdot5°$.

A month later unchanged.

$p = 4{\cdot}748$ in ether; $d_{20} = 0{\cdot}731$; $l = 1$ dcm.; a_D^{20} $+4{\cdot}933°$; $[a]_D^{20}$ $+142{\cdot}1°$.

$p = 10{\cdot}86$ in ether; $d_{20} = 0{\cdot}7465$; $l = 1$ dcm.; a_D^{20} $+11{\cdot}65°$; $[a]_D^{20}$ $+139{\cdot}2°$.

Diethyl Ester, $C_7H_{12}(CO_2Et)_2$.

B. p. 138—140°/12—13 mm.; $d_{19} = 1{\cdot}019$:

0·2064 gave 0·4861 CO_2 and 0·1690 H_2O. C = 64·23; H = 9·163.

$C_{13}H_{22}O_4$ requires C = 64·42; H = 9·157 per cent.

Rotatory power:

$d_{19} = 1{\cdot}019$; $l = 1$ dcm.; a_D^{19} $+116{\cdot}27°$; $[a]_D^{19}$ $+114{\cdot}1°$.

Four and a-half months later, $[a]_D$ $+114{\cdot}3°$.

$p = 5{\cdot}135$ in ether; $d_{18} = 0{\cdot}731$; $l = 1$ dcm.; a_D^{18} $+4{\cdot}35°$; $[a]_D^{18}$ $+115{\cdot}9°$.

$p = 10{\cdot}073$ in ether; $d_{18} = 0{\cdot}7437$; $l = 1$ dcm.; a_D^{18} $+7{\cdot}93°$; $[a]_D^{18}$ $+106°$.

Di-n-propyl Ester, $C_7H_{12}(CO_2Pr^a)_2$.

B. p. 157—160°/11—13 mm.; $d_{16/16} = 0{\cdot}9969$:

0·1664 gave 0·4039 CO_2 and 0·1531 H_2O. C = 66·20; H = 10·29.

$C_{15}H_{26}O_4$ requires C = 66·61; H = 9·699 per cent.

Rotatory power:

$d_{12} = 0{\cdot}9973$; $l = 1$ dcm.; a_D^{12} $+84{\cdot}5°$; $[a]_D^{12}$ $+84{\cdot}7°$.

$p = 6{\cdot}786$ in ether; $d_{17} = 0{\cdot}740$; $l = 1$ dcm.; a_D^{17} $+4{\cdot}28°$; $[a]_D^{17}$ $+85{\cdot}2°$.

Diisobutyl Ester, $C_7H_{12}(CO_2{\cdot}C_4H_9)_2$.

B. p. 174—176°/12—14 mm.; $d_{15} = 0{\cdot}9908$.

0·1725 gave 0·4258 CO_2 and 0·1502 H_2O. C = 67·32; H = 9·74.

$C_{17}H_{30}O_4$ requires C = 68·45; H = 10·14 per cent.

Rotatory power:

$d_{12} = 0{\cdot}991$; $l = 1$ dcm.; a_D^{12} $+76{\cdot}92°$; $[a]_D^{12}$ $+77{\cdot}62°$.

$p = 5{\cdot}577$ in ether; $d_{12} = 0{\cdot}7385$; $l = 1$ dcm.; a_D^{12} $+2{\cdot}95°$; $[a]_D^{12}$ $+71{\cdot}6°$.

$p = 13{\cdot}709$ in ether; $d_{12} = 0{\cdot}7610$; $l = 1$ dcm.; a_D^{12} $+7{\cdot}616°$; $[a]_D^{12}$ $+73{\cdot}0°$.

Diisoamyl Ester, $C_7H_{12}(CO_2{\cdot}C_5H_{11})_2$.

(The amyl alcohol used had a_D $-1{\cdot}1°$ in a 1-dcm. tube.)

B. p. 187—190°/10—12 mm.; $d_{15} = 0{\cdot}9924$:

0·2048 gave 0·5066 CO_2 and 0·1812 H_2O. C = 67·46; H = 9·897.

$C_{19}H_{34}O_4$ requires C = 69·88; H = 10·50 per cent.

Rotatory power:

$d_{15} = 0{\cdot}9924$; $l = 1$ dcm.; a_D^{15} $+72{\cdot}95°$; $[a]_D^{15}$ $+73{\cdot}5°$.

$p = 4{\cdot}4314$ in ether; $d_{16} = 0{\cdot}730$; $l = 1$ dcm.; a_D^{16} $+2{\cdot}366°$; $[a]_D^{6}$ $+73{\cdot}1°$.

Monobenzyl Ester, $CO_2H{\cdot}C_7H_{12}{\cdot}CO_2{\cdot}C_7H_7$.

B. p. 215—220°/12—14 mm.:

0·2311 gave 0·5931 CO_2 and 0·1492 H_2O. C = 69·99; H = 7·22.

$C_{16}H_{20}O_4$ requires C = 69·52; H = 7·30 per cent.

Rotatory power:

$p = 4{\cdot}566$ in ether; $d_{17} = 0{\cdot}735$; $l = 1$ dcm.; α_D^{17} $+1{\cdot}166°$; $[\alpha]_D^{17}$ $+34{\cdot}7°$.

Decomposition Products of the Sodio-derivative of the Dimethyl (or Diethyl) Ester of α-Thujadicarboxylic Acid.

On warming the sodio-derivative of the dimethyl ester with water, the odour of tanacetophorone was observed. In order to study this change, about 20 grams of ester were treated with metallic sodium, and the product distilled in a current of steam. The distillate, when treated with semicarbazide solution, gave at once a semicarbazone. This was carefully compared with the semicarbazone prepared from some tanacetophorone kindly furnished by Prof. Wallach, and their identity established. Both semicarbazones crystallise from methyl alcohol in shining leaflets, melting and decomposing at 187—188°. A mixture of the two semicarbazones behaves in the same way. The results of analysis were also in good agreement with theory:

0·1732 gave 0·3777 CO_2 and 0·1287 H_2O. C = 59·47; H = 8·31.

$C_9H_{15}ON_3$ requires C = 59·62; H = 8·35 per cent.

The semicarbazone was decomposed with oxalic acid and the tanacetophorone recovered. It showed the following constants: b. p. 215—217°; 99°/17—18 mm.; $d_{19/15} = 0{\cdot}9453$ (Semmler, *Ber.*, 1892, **25**, 3350, gives the following constants for tanacetophorone: b. p. 212—214°; 89—90°/13 mm.; $d_{20} = 0{\cdot}9378$).

The cooled residue remaining in the distillation flask was extracted with ether; the acid oil obtained in this way was dissolved in boiling water. After some time two acids slowly crystallised. These were mechanically separated and examined. Both were inactive. One melted at 116—117°, and was identical with β-thujadicarboxylic acid; the other melted at 150—151°. This was analysed:

0·1171 gave 0·2492 CO_2 and 0·0810 H_2O. C = 58·04; H = 7·73.

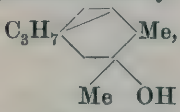
$C_9H_{14}O_4$ requires C = 58·03; H = 7·58 per cent.

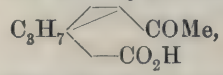
The *silver* salt was prepared:

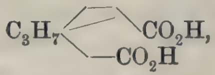
0·1172 gave 0·0634 Ag. Ag = 54·09.

$C_9H_{12}O_4Ag_2$ requires Ag = 53·97 per cent.

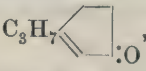
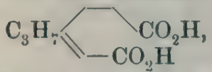
Summary.

Tanacetone (β-thujone), when treated with magnesium methyl iodide, yields two tertiary homothujyl alcohols,  one a solid, m. p. 84°, $[\alpha]_D$ $-30{\cdot}5°$; the other, a liquid, b. p. 204°, $[\alpha]_D$ $+35°$. In both these alcohols, as in thujyl alcohol, the *cyclo*propane ring is stable towards cold 5 per cent. sulphuric acid. The three next higher homologues of homothujyl alcohol are liquids. *iso*Thujone, when treated with magnesium methyl iodide in the same way, does not yield a solid tertiary alcohol.

α-Thujaketonic acid,  is decomposed by boiling with 20 per cent. hydrochloric acid with the formation of an unsaturated hydrocarbon (b. p. 160—165°), probably dihydro-ψ-cumene.

α-Thujadicarboxylic acid,  prepared from α-thujaketonic acid by oxidation, is quite stable towards boiling 20 per cent. hydrochloric acid and boiling 10 per cent. sodium hydroxide.

α-Thujadicarboxylic acid can be easily esterified in the ordinary way. *Dimethyl*, *diethyl*, *di*-n-*propyl*, *di*iso*butyl*, and *di*iso*amyl* esters have been prepared. All are colourless, odourless liquids.

The dimethyl and diethyl esters of α-thujadicarboxylic acid give a sodio-derivative, the decomposition products of which are tanacetophorone,  , β-thujadicarboxylic acid,  and an unknown inactive dicarboxylic acid, $C_9H_{14}O_4$, melting at 150—151°.

Chemical Laboratory,
The University,
Glasgow.

CXL.—*Optically Active Methoxysuccinic Acid from Malic Acid.*

By THOMAS PURDIE, F.R.S., and GEORGE BALLINGALL NEAVE, M.A., D.Sc.

OPTICALLY active monoalkyloxysuccinic acids were obtained a number of years ago (Trans., 1893, **63**, 217, and succeeding papers) by the resolution of the corresponding inactive acids with the aid of alkaloids. The inactive acids were prepared from fumaric esters, which possess the property of combining with the elements of alcohols under the action of sodium alkyloxides.

Later, in the course of our first experiments on alkylation by means of dry silver oxide and alkyl iodides (Trans., 1899, **75**, 157), it was shown that ethyl *l*-ethoxysuccinate could be prepared from ethyl malate. The yield of the pure ester, however, was unsatisfactory, as the product contained much unaltered malate, which was removed by treating the mixture with cold potassium hydroxide solution. This process naturally results in a diminished yield of alkylated product, as compared with the method of repeated alkylation which is now adopted. We have now employed the method referred to for the preparation of the methyl, ethyl, and propyl esters of *l*-methoxysuccinic acid with the view of controlling and extending the polarimetric observations made formerly (*loc. cit.*) on the compounds obtained by resolution of the inactive acid.

We find that the esters of *l*-methoxysuccinic acid are easily obtained in the pure state by methylating the corresponding malic esters, provided that a sufficient excess of the alkylating agent is used. Some oxidation occurs in the course of the action, but the oxidation products are readily removed by subsequent fractional distillation. In preparing *methyl* l-*methoxysuccinate*, dry silver oxide (2 mols.) was added in small quantities at a time to a mixture of methyl malate (1 mol.) and methyl iodide (4 mols.), and after all the oxide had been added and spontaneous action had ceased, the mixture was heated for two hours on a water-bath. The liquid product was extracted from the silver residues by means of ether, and after being dried with sodium sulphate and freed from ether, was fractionated under diminished pressure. Twenty-five grams of methyl malate ($\alpha^{20°}$ $-8{\cdot}36°$; $l=1$) gave, after the first distillation, 22 grams of the methylated ester boiling at 113—114°/15 mm., and showing the observed rotation $\alpha_D^{20°}$ $-61{\cdot}74°$ ($l=1$). After three more distillations, the rotation was constant at $-62{\cdot}79°$, and was not altered by repeating the methylation.

The active methyl methoxysuccinate, formerly prepared by resolution of the inactive acid (Trans., 1895, **67**, 970), was the ester of the *d*-acid. The antipodal forms are liquid, and could not be solidified by cooling. The inactive ester obtained from methyl fumarate (Trans., 1891, **59**, 469), on the other hand, is crystalline, and melts at 28°. On mixing equal weights of the two oppositely active esters derived as above described from different sources and cooling the mixture to 0°, crystallisation did not occur spontaneously, but on adding a nucleus of the inactive form the whole mass quickly solidified. After being again melted, the mixture solidified spontaneously at the ordinary temperature, and now melted at the same temperature as the inactive substance, 28°.

Ethyl l-*methoxysuccinate* was prepared from ethyl malate (α^{20° −11·76°, $l=1$) in the same manner as the methyl ester. The *propyl* ester was prepared by the action of propyl iodide on the silver salt obtained from methyl *l*-methoxysuccinate. The results of analysis and the polarimetric and other observations made on the liquid esters are recorded below.

Methyl l-*methoxysuccinate*, b. p. 113—114°/15 mm.:

Found, C = 47·46; H = 7·08.

$C_7H_{12}O_5$ requires C = 47·73; H = 6·82 per cent.

Ethyl l-*methoxysuccinate*, b. p. 126°/17 mm.:

Found, C = 52·88; H = 7·84.

$C_9H_{16}O_5$ requires C = 52·94; H = 7·84 per cent.

Propyl l-*methoxysuccinate*, b. p. 145—146°/12 mm. The *silver* salt obtained from the product of hydrolysis of methyl *l*-methoxysuccinate, which was used in preparing this ester, gave:

Found, C = 16·45; H = 1·90; Ag = 59·58.

$C_5H_6O_5Ag_2$ requires C = 16·58; H = 1·66; Ag = 59·65 per cent.

The observations from which the molecular rotations, recorded below, are calculated were taken in a 1-dcm. tube.

l-*Methoxysuccinic Esters* (*Pure Liquids*).

	d 20°/4°.	$[M]_D^{20^\circ}$.	*d* 40°/4°.	$[M]_D^{40^\circ}$.	*d* 60°/4°.	$[M]_D^{60^\circ}$.	t*[α] 20—60°.
Methyl...	1·1415	−96·8°	1·1199	−95·6°	1·0983	−93·9°	−0·0008
Ethyl ...	1·0676	102·9	1·0476	101·5	1·0273	100·1	−0·0007
Propyl ...	1·0312	109·0	1·0101	107·3	0·9908	105·6	−0·0008

* Temperature-coefficient, as defined by Walden (*Ber.*, 1905, **38**, 363).

The polarimetric observations on solutions of the three esters, from which the molecular rotations recorded in the following tables are calculated, were taken in a 2-dcm. tube at 20°. The concentrations by volume (*c*) were determined from the specific gravities of the solutions (*d* 20°/4°) and the concentrations by weight. The specific gravities (*d* 20°/4°) of the benzene and ethyl alcohol used in the case of the methyl and ethyl esters were 0·8785 and 0·7912 respectively; those of the solvents used in the case of the propyl ester were 0·8789 and 0·7910 respectively. The molecular solution volumes (M.S.V.) were calculated by the usual formula.

Methyl l-*Methoxysuccinate.*

$[M]_D^{20°}$ −96·8°, *d* 20°/4° 1·1415, *M*/*d* 154·2.

Solvent.	*c.*	*d* 20°/4°.	$[M]_D^{20°}$.	M.S.V.
Benzene	19·9734	0·9238	−114·7°	154·9
	10·0175	0·9012	118·1	154·9
	5·0399	0·8899	120·0	155·0
Ethyl alcohol ...	20·0056	0·8533	−90·6	153·4
	10·0456	0·8225	90·2	153·1
	5·0038	0·8070	91·1	152·2

Ethyl l-*Methoxysuccinate.*

$[M]_D^{20°}$ −102·9°, *d* 20°/4° 1·0676, *M*/*d* 191·1.

Solvent.	*c.*	*d* 20°/4°.	$[M]_D^{20°}$.	M.S.V.
Benzene	20·0429	0·9138	−118·2°	191·3
	10·0090	0·8962	120·4	191·1
	5·0339	0·8872	123·4	192·1
Ethyl alcohol...	19·9254	0·8434	−96·2	190·3
	9·9748	0·8174	97·3	190·1
	5·0263	0·8045	97·6	189·6

Propyl l-*Methoxysuccinate.*

$[M]_D^{20°}$ −109·0°, *d* 20°/4° 1·0312, *M*/*d* 225·0.

Solvent.	*c.*	*d* 20°/4°.	$[M]_D^{20°}$.	M.S.V.
Benzene	19·9105	0·9082	−122·3°	225·1
	10·0140	0·8935	125·7	225·5
	4·9880	0·8865	126·7	223·7
Ethyl alcohol ...	19·8346	0·8376	−101·1	224·4
	10·0320	0·8149	101·1	223·4
	6·0014	0·8054	100·1	222·9

The optically active diamide and dianilide of methoxysuccinic acid, which have not been hitherto examined, were readily obtained from methyl *l*-methoxysuccinate by the action of methyl-alcoholic ammonia solution at the ordinary temperature, and of aniline at 130—140° respectively. The analysis of these compounds and the results of polarimetric observations ($l=2$) made on their solutions are recorded below. The molecular rotations of maldiamide and maldianilide are appended for comparison.

l-*Methoxysuccindiamide* crystallises from methyl-alcoholic solution in prisms melting at 178—179°. The inactive amide melts at 175° (Trans., 1891, **59**, 471):

Found, C = 41·13; H = 7·01; N = 19·33.

$C_5H_{10}O_3N_2$ requires C = 41·10; H = 6·85; N = 19·18 per cent.

l-*Methoxysuccindianilide* crystallises from hot benzene solution in small needles, melting at 158—159°:

Found, N = 9·58.

$C_{17}H_{18}O_3N_2$ requires N = 9·40 per cent.

Solvent.	*l*-Methoxy-succindiamide.		Maldiamide.	*l*-Methoxy-succindianilide.		Maldianilide.
	c.	$[M]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.	*c*.	$[M]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
Water	7·4860	−59·4°	−50·2°*	—	—	—
,,	1·2165	58·8	—	—	—	—
Methyl alcohol	1·0460	83 0	—	2·1096	−231·7°	—
Acetic acid	3·9954	60·8	59·7 †	2·1193	158·9	−172·3°*
,,	2·0333	60·7	—	1·5408	158·6	—
Pyridine	0·2740	117·2	76·2 †	2·4546	197·9	287·1 ‡
,,	—	—	—	1·2063	196·4	—

* Walden, *Zeitsch. physikal. Chem.*, 1895, **17**, 265.

† McCrae, Trans., 1903, **83**, 1326.

‡ Guye and Babel, *Arch. Sci. phys. nat.*, 1899, [iv], **7**, 23.

The observation on methoxysuccindianilide in methyl-alcoholic solution was made at 16°. Methoxysuccindiamide being very sparingly soluble in pyridine, the rotation given for it in this solvent is only approximate.

Discussion of Results.

Considering the uncertainty of obtaining active compounds displaying the maximum rotation by the methods of resolution, the rotatory powers of the esters formerly obtained from *dl*-methoxysuccinic acid are in fair agreement with the more exact values now found for the same compounds obtained from malic acid. It was stated (Trans., 1895, **67**, 979) that the value there recorded for methyl *d*-methoxysuccinate was probably about 2° low, and that the actual value should therefore be about $[\alpha]_D^{12^\circ}$ +54·5°. The value now found for the *l*-ester from malic acid, corrected for temperature, is $[\alpha]_D^{12^\circ}$ −55·27°. The values for the ethyl *l*-ester from the two different sources are $[\alpha]_D^{18^\circ}$ −50·11° and −50·51° respectively, and for the propyl *l*-ester, $[\alpha]_D^{15^\circ}$ −45·21° and −47·19°. The *l*-methoxysuccinic acid, now obtained by hydrolysing the methyl *l*-ester from methyl malate, gave in aqueous solution for *c* = 6·135, $[\alpha]_D^{15^\circ}$ −33·56°; the *d*-acid from the alternative source (Trans., 1893, **63**, 224) in approximately the same concentration gave $[\alpha]_D^{18^\circ}$ +33·04°.

The optical relationships of the methyl, ethyl, and propyl *l*-monomethoxysuccinates resemble those of the corresponding *d*-dimethoxysuccinates already described (Purdie and Irvine, Trans., 1901, **79**, 963), and a general parallelism is observable in the relationships of each series to the parent malic and tartaric series. We tabulate below the molecular rotations of the four series of liquid esters. Observations at 20° being impossible in the case of methyl *d*-dimethoxysuccinate (m. p. 53°), values at 60° are given for all the methoxysuccinates; the values* of the tartrates and dimethoxy-derivatives have been halved, so as to exhibit the optical effect of only one of the two asymmetric groups. The intermediate columns show the differences between the molecular rotations of the methylated esters and the corresponding malates (Walden, *loc. cit.*) and tartrates (Pictet, *Jahresber.*, 1882, 856):

	l-Monomethoxy-succinates. $[M]_D^{60°}$.	Diff.	Malates. $[M]_D^{20°}$.	*d*-Dimethoxy-succinates. $[M]_D^{60°}/2$.	Diff.	Tartrates. $[M]_D^{20°}/2$.
Methyl ...	−93·9°	82·8°	−11·1°	+85·0°	83·1°	+1·91°
Ethyl ...	100·1	80·8	19·3	99·9	92·0	7·89
Propyl ...	105·6	80·3	25·3	106·3	91·8	14·55

It is seen from the tabulated figures that the methylation of malic and tartaric esters produces a remarkable increase of rotatory power in the lævo- and dextro-sense respectively. The alkyl radicles when introduced into these esters have, in fact, a much greater effect in the directions indicated than any of the acyl groups. It has been previously pointed out (Purdie and Irvine, *loc. cit.*) that, regarding the malic esters as derived from *d*-malic acid, the radicles in respect of their optical influence as substituents in the cases under consideration may be said to stand at the positive, the aromatic acyl groups at the negative, end of the scale, whilst the aliphatic acyl groups hold an intermediate position.

The ethereal mono- and di-methoxysuccinates, like the parent malates and tartrates, exhibit an increase of rotatory power with ascent of the series. Inspection of the columns of differences shows that the optical effect of methylating the three malates is remarkably constant, raising the rotation of each by about the same amount (80° to 83°). The rise produced in the case of ethyl and propyl tartrates is also uniform, although considerably greater (about 92°), the result being that despite the lower activity of the tartrates * as compared with the malates, ethyl and propyl dimethoxysuccinates show nearly the same values as the corresponding monomethoxy-esters. The optical effect of methylating methyl tartrate, however, diverges considerably from the regularity exhibited by the other malates and tartrates. The molecular rotation of methyl dimethoxysuccinate is about 9° short of that of methyl monomethoxysuccinate, the increase of rotation produced by the methylation of methyl tartrate being only 83·1°. This exceptional result may be related to the fact that, whilst methyl monomethoxysuccinate is liquid even at 0°, the dimethoxysuccinate at the temperature of observation (60°) is but little removed from its melting point, and is therefore possibly in a state of abnormal aggregation.

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* As stated above, the halved molecular rotations of the tartrates and the dimethoxy-derivatives are here referred to.

The rotatory powers of the mono- and di-methoxysuccinic esters are similarly influenced by (1) change of temperature, (2) solvents, (3) concentration in solutions. Certain regularities with respect to the influence of these factors are also observable in comparing malates and tartrates with the mono- and di-methylated esters respectively, but the relationships here become extremely complex, and require more extended investigation for their elucidation. With some exceptions, the optical effect of the three factors on the methoxy-esters is in the opposite sense to their effect on the parent hydroxy-esters.

With rise of temperature, within the limits of our observations, the mono- and di-methoxysuccinates examined show a diminution, the corresponding malates and tartrates, like lactates and glycerates (Walden, *Ber.*, 1905, **38**, 364), an increase of rotatory power. The temperature-coefficients (p. 1518) of the three monomethoxy-esters have nearly the same value (−0·0008), and those of the ethyl and propyl dimethoxy-esters (−0·0014 and −0·0012) do not differ very greatly from them. It is noteworthy that the abnormal sensitiveness to temperature which characterises the tartaric esters (Walden, *loc. cit.*) disappears when they are methylated.

All the three esters of the mono- and di-methoxysuccinic series (Trans., 1901, **79**, 973) show a marked rise in the value of $[M]_D^{20°}$ when dissolved in benzene ($c = 20$ per cent.). A further rise occurs on dilution ($c = 5$ per cent.). A fall in value, much less in amount, is produced by solution of the monomethoxysuccinates in ethyl alcohol, and the same result holds for solution of the methyl and ethyl dimethoxysuccinates in methyl alcohol. The relationships of the dimethoxysuccinates with the tartrates in respect of the influence of solvents on their rotatory powers have been previously described (*loc. cit.*). With regard to the monomethoxysuccinates and the parent malates, the effects of benzene and of methyl alcohol on methyl and ethyl malates (Walden, *Ber.*, 1906, **39**, 671) are again in the opposite sense to their effects on the corresponding methylated esters.

The well-known researches of Patterson have shown that in many instances a correspondence can be traced between changes of rotation and of molecular solution volume. Our observations on the three ethereal *l*-methoxysuccinates exhibit some regularities in this connexion, which may be recorded. The increase of molecular rotation produced by solution of the esters in benzene is attended by a parallel increase of molecular volume. The initial increments of molecular rotation on dissolving the compounds in benzene ($c=20$ per cent.) are 17·9°, 15·3°, and 13·3° for the methyl, ethyl, and propyl terms respectively. The corresponding increments of molecular volume (0·7, 0·2, and 0·1) are small, but obviously diminish, like the increments of rotation, with ascent of the series. The further increase of rotation which occurs on diluting the benzene solutions is associated with a further slight increase of molecular solution volume. The molecular solution volume of the propyl ester, however, shows a maximum at the concentration $c=10$ per cent., and a corresponding maximum of rotation might be expected at this point. Although no such maximum occurs, the smaller increase of rotation exhibited by this ester in the most dilute solution, when compared with the corresponding increases shown by the methyl and ethyl esters, indicates that its rotations are more nearly approaching a maximum.

As already stated, the initial effect of ethyl alcohol, in contradistinction to that of benzene, is a diminution of rotation; the effect of alcohol on molecular volume is also in the opposite sense to that of benzene. The changes which occur on diluting the alcoholic solutions do not show, however, any obvious connection between rotation and molecular solution volume.

The rotatory powers of malamide and tartramide and their derivatives have been systematically investigated by Frankland and his pupils in recent years (Trans., 1906, **89**, 1859; 1910, **97**, 154, and preceding papers). In both the malic and tartaric series, the aromatic amides show a much higher molecular rotation than the unsubstituted amides and alkylamides. Our observations on *l*-methoxysuccinamide and anilide in methyl alcohol and glacial acetic acid solutions (p. 1520) show that here also a great increase attends the introduction of a phenyl group into the simple amide.

A general similarity also prevails with respect to the influence of different solvents on the rotatory powers of maldiamide and maldianilide on the one hand, and of the corresponding methoxy-derivatives on the other. Disregarding the effect of methyl alcohol, for which in the case of malamide no data are available, the values of both the diamides are at their lowest in water, and at their highest in pyridine solution. The rotations of both anilides are much higher in pyridine than in acetic acid solution.

It is particularly worthy of notice that the replacement of the group CH·OH by CH·OMe, which so largely enhances the rotatory power in the case of malic acid and its esters, has not the similar effect in the case of the amide and anilide of malic acid, which was to be expected. The rotation of *l*-methoxysuccinamide, it is true, exceeds that of malamide in pyridine solution, and by a relatively small amount also in water solution, but the rotations of the methoxy-amide and anilide in the other solvents are either about equal to those of the corresponding unsubstituted malic compounds, or distinctly lower.

The metallic salts are the only other derivatives of malic acid, so far known, whose rotation is lowered by the alkylation of the alcoholic hydroxyl group.

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CXLI.—*Optically Active Derivatives of* l-*Methoxy- and* d-*Dimethoxy-succinic Acids.*

By THOMAS PURDIE, F.R.S.; and CHARLES ROBERT YOUNG, B.Sc.

IN continuation of previous work (see p. 1517 and Trans., 1901, **79**, 957), we have prepared a number of derivatives of optically active mono- and di-methoxysuccinic acids, an account of which is contained in the following paper.

In view of the superior stability of the alkyloxy-group as compared with the hydroxyl group, it appeared probable that derivatives, such as acid chlorides and anhydrides, which cannot be obtained from malic or tartaric acids, could be prepared from the corresponding alkyloxy-acids. Derivatives of this nature should prove useful in the synthesis of optically active substances, and also for comparing the optical relationships of compounds of the succinic acid type.

We find that the methoxyl groups are, in general, not affected by the reagents used, and that the products are optically active, the only cases exceptional in this respect being the action of sodium methoxide and of magnesium phenyl bromide on methyl *l*-methoxysuccinate.

The chlorides and anhydrides of the mono- and di-methoxysuccinic acids are readily obtained from the corresponding acids by the action of phosphorus pentachloride and acetyl chloride respectively. The monomethoxy-compounds are both liquids which distil without decomposition; the dimethoxy-compounds are crystalline.

The constitution of succinyl chloride has been the subject of much discussion. In certain well-defined cases the compound reacts in the lactonic form; recently Meyer and Marx have shown conclusively (*Ber.*, 1908, **41**, 2459) that with alcohols, on the other hand, it acts as if it had the ordinary constitution of an acid chloride. The substance is therefore tautomeric, but there is no satisfactory evidence to show whether it consists of one only of the two desmotropic forms or of a mixture of both.

We have not yet applied the reactions to mono- and di-methoxysuccinyl chlorides, which on the analogy of succinyl chloride should give derivatives of the lactonic type. We find, however, that with alcohols they react like succinyl chloride in the ordinary symmetric form. A specimen of the liquid methyl *l*-methoxysuccinate, obtained by interaction of the chloride and methyl alcohol, was practically identical in rotatory power with the ester prepared from the silver salt of the acid (Trans., 1895, **67**, 970), and also with that obtained by the methylation of methyl malate. Similarly, the crystalline methyl *d*-dimethoxysuccinate obtained from the corresponding acid chloride was identical in melting point and rotatory power with the product of methylation of methyl tartrate.

Moreover, we find that the polarimetric examination of solutions of these chlorides in indifferent solvents shows that the compounds exist in one form only, judging from the fact that the rotatory powers remain permanent under conditions which usually promote tautomeric change. Thus, a benzene solution of *l*-methoxysuccinyl chloride showed no mutarotation after forty-eight hours. The rotation of a similar solution of *d*-dimethoxysuccinyl chloride, to which a trace of aluminium chloride * was added as a catalytic agent, remained unchanged after the lapse of six weeks. In another experiment a fresh quantity of the crystalline chloride was heated in a sealed tube at 100° for six hours in the fused state. This treatment produced no change in the melting point of the solidified substance or in its rotatory power in benzene solution, and no mutarotation occurred on addition of a trace of aluminium chloride and on prolonged keeping. The same observations were made on the compound immediately after being distilled, with the same negative results. We conclude from these experiments that, whatever be the case with succinyl chloride, its methoxy-derivatives are not mixtures of dynamic isomerides.

The methyl hydrogen esters of *l*-mono- and *d*-di-methoxysuccinic acids were readily obtained from the respective anhydrides by heating these with methyl alcohol. Both compounds are crystalline.

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* Aluminium chloride was used as, with this reagent and benzene, succinyl chloride is known to react in the lactonic form.

By passing dry ammonia gas into *l*-methoxysuccinic anhydride at 100°, a mixture of the amic acid and its ammonium salt was produced, from which the former was isolated by fractional crystallisation. The dry distillation of the amic acid gave a crystalline substance (melting point 59—61°), which analysis showed to have the composition of the imide, but lack of material prevented further examination.

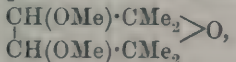
The action of alcoholic sodium methoxide on methyl *l*-methoxysuccinate was undertaken in the hope of obtaining an optically active dimethoxysuccinylosuccinic ester. Condensation occurred, but the reaction was more complex than in the case of the unsubstituted succinic ester, one at least of the etheric methoxyl groups of the two condensing molecules being lost and the optical activity destroyed. The only product isolated was a pale yellow, amorphous solid, which in alcoholic solution gave a plum coloration with ferric chloride, changing to reddish-purple on dilution. It could not be crystallised, nor could crystalline derivatives be obtained from it. Combustion and estimation of methoxyl agreed with figures calculated for a closed-ring condensation of two molecules of methyl methoxysuccinate with the loss of three molecules of methyl alcohol, or for the isomeric substance which would result from an open-chain condensation of two molecules of methyl fumarate by the abstraction of one molecule of methyl alcohol. In general properties and in composition, it was identical with a condensation product previously obtained (Trans., 1891, **59**, 472) from the action of alcoholic sodium methoxide on methyl fumarate. The substance appears to be of some interest, and will be examined later.

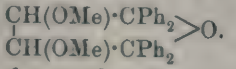
Valeur (*Compt. rend.*, 1901, **132**, 833; *Bull. Soc. chim.*, 1902, [iii], **27**, 1138; 1903, [iii], **29**, 683), Dilthey and Last (*Ber.*, 1904, **37**, 2639), and others have shown that Grignard reagents act normally on succinic esters, producing ditertiary glycols, and in some cases anhydrides of the glycols (Acree, *Amer. Chem. J.*, 1905, **33**, 180). The reaction with alkyloxysuccinic esters follows the same course, the products being the corresponding optically active mono- and di-alkyloxyglycols or their anhydrides. The action of magnesium phenyl bromide on methyl methoxysuccinate is, however, more complex, and is described in the succeeding paper.

With magnesium methyl iodide, methyl *d*-dimethoxysuccinate ($[\alpha]_D$ +81·04° in methyl alcohol solution) gave lævorotatory *γδ-dimethoxy-βε-dimethylhexane-βε-diol*,

$$HO\cdot CMe_2\cdot CH(OMe)\cdot CH(OMe)\cdot CMe_2\cdot OH$$

(m. p. 71°, $[\alpha]_D$ −30·9° in methyl-alcoholic solution). On treating the substance with excess of dry silver oxide and methyl iodide in the usual manner, the hydroxyl groups were only very partly methylated. In view of our experience with this alkylation process, the result was a matter of surprise, but it appears that tertiary alcohols resist alkylation by this method. G. D. Lander (Trans., 1900, **77**, 732) found this to be the case with triphenylcarbinol, and A. McKenzie and H. Wren (Trans., 1910, **97**, 476) have shown that of the two hydroxyl groups of *l*-triphenylethylene glycol, the secondary alcoholic group only is thus methylated.

On distilling the lævorotatory glycol repeatedly under the ordinary pressure, it was converted to a large extent into a dextrorotatory liquid anhydride by the loss of one molecule of water. βε-Dimethylhexane-βε-diol (L. Henry, *Compt. rend.*, 1906, **143**, 496) gives the unsaturated alcohol, $\mathrm{CMe_2{:}CH\cdot CH_2\cdot CMe_2\cdot OH}$, by dry distillation. It is unlikely, however, that dehydration should occur in this fashion in the case of the corresponding dimethoxy-glycol, and the dextrorotatory liquid referred to above is more probably the furan derivative,  $\left.\begin{array}{l}\mathrm{CH(OMe)\cdot CMe_2}\\ \mathrm{CH(OMe)\cdot CMe_2}\end{array}\right>\mathrm{O}$, ring formation having changed the sign of rotation.

With magnesium phenyl bromide, ethyl succinate gives tetraphenyltetramethylene glycol (*ααδδ* - tetraphenylbutane - *αδ* - dione) under ordinary conditions, but Acree (*loc. cit.*) found that with a boiling ethereal solution of the Grignard reagent the only product of the reaction was an anhydride, probably tetraphenyltetramethylene oxide (2 : 2 : 5 : 5-tetraphenyltetrahydrofuran). In our experiments on the action of magnesium phenyl bromide on methyl *d*-dimethoxysuccinate, the reaction mixture was not heated, but an excess of the Grignard reagent was used, and the only product isolated was an anhydride (m. p. 184—185°) of the expected glycol. The compound decolorised alkaline permanganate in the cold only after a long time, and did not combine with bromine; we conclude therefore that it is 3 : 4-*dimethoxy*-2 : 2 : 5 : 5-*tetraphenyltetrahydrofuran*,  $\left.\begin{array}{l}\mathrm{CH(OMe)\cdot CPh_2}\\ \mathrm{CH(OMe)\cdot CPh_2}\end{array}\right>\mathrm{O}$. The compound is thus the dimethylated oxide of tetraphenylerythritol,

$$\mathrm{HO\cdot CPh_2\cdot CH(OH)\cdot CH(OH)\cdot CPh_2\cdot OH},$$

which Frankland and Twiss (Trans., 1904, **85**, 1666) obtained by the action of magnesium phenyl bromide on methyl tartrate. Frankland's glycol is strongly dextrorotatory ($[\alpha]_D$ +182·8° in ethyl-alcoholic solution); our compound is lævorotatory ($[\alpha]_D$ − 115·7° in benzene solution). The great difference between the rotatory powers of the two compounds is probably attributable in the main to the existence of the ring in the structure of the oxide.

Optical Rotatory Powers.

All the mono- and di-alkyloxysuccinic acids and their derivatives, which have been examined, excepting some salts of bivalent metals and the products of the Grignard reactions, retain the sign of the parent *l*-malic and *d*-tartaric acids, that is to say, the monoalkyloxy-compounds are lævorotatory, the dialkyloxy-compounds dextrorotatory. The rotatory powers are much influenced by the nature of the solvent used, water giving as a rule the lowest, and benzene the highest values. The order of increasing effect on the values is in general as follows: water$<$methyl and ethyl alcohols$<$acetone $<$benzene. We tabulate below in the form of molecular rotations some of the observations recorded in the experimental part of this and the preceding paper, and in earlier communications (Trans., 1895, **67**, 949, 979; 1901, **79**, 962, 965); also, the results of some unpublished observations. To present the results in comparable form, the molecular rotations of the tartrate derivatives have been halved so as to show the optical effect of one only of the two similar asymmetric groups, and in case of solutions, observations have been selected where concentrations were approximately similar, so far as the available data permitted.

l-*Malic derivatives.*

	Solvent.	$[M]_D^{20°}$.
l-Methoxysuccinic :		
Acid	Acetone	$-88·9°$
Chloride	Benzene	100·2
Anhydride	Acetone	109·1
Dimethyl ester.	Pure liquid	93·9
Diethyl ,,	,,	102·9
Dipropyl ,,	,,	109·0
l-Ethoxysuccinic :		
Dimethyl ester.	,,	115·9
Diethyl ,,	,,	121·0
Dipropyl ,,	,,	126·1

d-*Tartaric derivatives.*

	Solvent.	$[M]_D^{20°}/2$.
d-Dimethoxysuccinic :		
Acid	Acetone	$+85·2°$
Chloride	Benzene	111·9
Anhydride	Acetone	119·0
Dimethyl ester.	Pure liquid	85·0
Diethyl ,,	,,	105·3
Dipropyl ,,	,,	111·2
d-Diethoxysuccinic :		
Dimethyl ester.	,,	106·4
Diethyl ,,	,,	124·3
Dipropyl ,,	,,	125·3

Dimethyl methoxysuccinate is liquid, dimethyl dimethoxysuccinate solid (m. p. 52—53°). The values given for these esters are therefore for 60°. The former ester has $[M]_D^{20°}$ $-96·8°$; the value calculated for the latter should be about $+90°$ at 20°.

In both series the conversion of acid into anhydride is attended by extensive change of rotatory power, as is commonly the case in ring formation. The acids, it will be seen, are the least optically active of the compounds mentioned, whilst the anhydrides show values of the same order as the more active esters. The conversion of acid into chloride also raises the rotation, but to a less extent. The value for dimethoxysuccinyl chloride, namely 85·8°, is, in fact, but little higher than that for the acid in the same solvent. With respect to the direction of the change of rotation attending the conversion of acid into chloride, ester, and anhydride, optically active acids of the succinic type show a general regularity which may be stated thus: the changes of rotatory power attending the conversion of alkyloxy-, acyloxy-, and halogen-succinic acids of the same configuration into chloride, ester, or anhydride are similarly directed, the rotation of the *d*- and *l*-acids being always shifted in the dextro- and lævo-direction respectively. Keeping in view the fact that *l*-malic and *d*-tartaric acids have an opposite configuration, the rotations of the acids derived from the former are accordingly shifted by the conversions mentioned in the lævo-direction, the rotations of those derived from the latter in the dextro-direction. The regularity in question is illustrated in the preceding and following tables. The values quoted below are molecular rotations calculated from specific rotations to be found in Long's translation of Landolt's "Optical Rotating Power." The value given for *l*-bromosuccinic acid is taken from Walden's observation on its enantiomorph, and those for acetylmalic acid and its anhydride from Pictet (*Compt. rend.*, 1893, **116**, 1134). Where no solvent is indicated, the observations refer to the pure liquid:

$[M]_D$.

	Acid.	Chloride.	Ethyl ester.	Anhydride.
l Acetylmalic	−37° to −45·4° Acetone.	——————→	−52·2°	→ −41·1° Chloroform.
l-Chlorosuccinic	+80·3° Ethyl acetate.	→ +55·9°	→ +57·3°	→ +41·5° Ethyl acetate.
l-Bromosuccinic	+133·8° Ether.	——————→	+103·6°	
d-Diacetyltartaric...... .	−55·3° Ethyl alcohol.	——————→	+14·5°	→ +126·8° Benzene.
d-Dibenzoyltartaric	−417·0° Ethyl alcohol.	——————→	−245·7°	→ +486·0° Acetone.

The only exception to the general uniformity shown in the table is the low rotation of *l*-acetylmalic anhydride, but this is doubtless explained by the lowering influence of the solvent used (see Walden's observation on methyl acetylmalate in chloroform solution, *Ber.*, 1906, **39**, 675). The dextrorotatory halogen-succinic acids are now recognised to have the same configuration as *l*-malic acid, and the direction of the changes of rotation is in agreement with this view.

The direction of the change of rotation in passing from acid to ester in the case of malic and tartaric acids also follows the rule stated. Malic esters are more lævorotatory than malic acid. The molecular rotation of tartaric acid in dilute aqueous solution, it is true, is higher than that of pure ethyl tartrate, but the values found under such different conditions are not comparable. The ester is more dextrorotatory than the acid when both are examined in aqueous solution, or when the acid in organic solvents is compared with the liquid ester. Tartaric acid is, in fact, lævorotatory in a mixture of acetone and ether.

We have previously drawn attention (Trans., 1901, **79**, 964) to the unexpected general similarity of the molecular rotations of corresponding mono- and di-alkyloxysuccinic esters. The similarity is remarkable in view of the divergent rotations of malic and tartaric esters, and of their respective mono- and di-acyl derivatives. Fresh data included in the table illustrate still further the regularity referred to. It will be seen that in the case of the esters, and of the acids in acetone solution, the correspondence of the values of the mono- and di-alkyloxy-compounds is remarkably close, that is to say, the introduction of OR into $CH_2{\cdot}CO_2R$ or into $CH_2{\cdot}CO_2H$ produces remarkably little change on the optical effect of the asymmetric group. The only exceptions are the commonly irregular methyl esters of the series, in which the substitution produces a decided fall of rotation. In general, the introduction of the second alkyloxy-radicle is attended by a slight rise of the value. The considerable rise noticeable in the case of the acids, chlorides, and anhydrides is possibly related to the accompanying change of molecular aggregation, the monomethoxy-compounds being liquids, and the dimethoxy-compounds solids at the ordinary temperature.

EXPERIMENTAL.

The *l*-methoxysuccinic acid used in the following preparations was obtained from methyl malate by the methods already described (p. 1517).

l-*Methoxysuccinyl Chloride.*—To 11 grams (1 mol.) of dry *l*-methoxysuccinic acid, 80 c.c. of benzene and 40 grams (2·5 mols.) of phosphorus pentachloride were added, and the mixture was heated for two hours on a water-bath under a reflux condenser. After distilling off benzene and phosphoryl chloride under diminished pressure, the residual liquid gave, on repeated fractionation, 5·7 grams of liquid distillate, b. p. 114—117°/56 mm.:

Found, Cl = 37·02.

$C_5H_6O_3Cl_2$ requires Cl = 38·33 per cent.

The rapid decomposition of the chloride when exposed to moist air accounts for the low analytical result. The persistence of the methoxyl group in the acid chloride was confirmed by treating it with methyl alcohol, when methyl *l*-methoxysuccinate was produced.

The specific rotation, $-51{\cdot}9^\circ$, of an acetone solution of the crude, once distilled ester so obtained agreed fairly with that of the initial ester, $-53{\cdot}1^\circ$, prepared from methyl malate. When warmed with water, the chloride dissolved gradually, and, on evaporation, the initial crystalline acid was recovered. The specific rotation of the acid chloride in benzene solution was $[\alpha]_D^{20^\circ}$ $-54{\cdot}18^\circ$, $c=6{\cdot}4317$.*

The chloride was also prepared by the combined action of acetyl chloride and phosphorus pentachloride on the acid, and the product showed practically the same rotatory power, namely, $-54{\cdot}08^\circ$, $c=5{\cdot}0667$, but in some experiments this method gave a mixture of chloride and anhydride, which had to be separated by fractional distillation.

l-*Methoxysuccinic Anhydride.*

This compound was obtained by heating the dry acid with about four times its weight of acetyl chloride, and distilling the product under diminished pressure. Thirty-one grams of acid gave 22 grams of the crude anhydride, from which, after repeated fractionation, 11 grams of the pure liquid were collected (b. p. 130—132°/17 mm.). Analysis gave:

Found, $C=45{\cdot}92$; $H=4{\cdot}73$; $OMe=24{\cdot}29$.

$C_4H_3O_3(OMe)$ requires $C=46{\cdot}13$; $H=4{\cdot}66$; $OMe=23{\cdot}86$ per cent.

In acetone solution, $[\alpha]_D^{20^\circ}$ $-83{\cdot}91^\circ$, $c=5{\cdot}6783$, and in benzene solution, $-103{\cdot}3^\circ$, $c=4{\cdot}9973$.

Methyl Hydrogen l-*Methoxysuccinate.*

On boiling a methyl-alcoholic solution of the anhydride, and distilling the product, the acid ester was obtained as a strongly acid oil (b. p. about 145°/10 mm.), which after some time suddenly crystallised. It was very soluble in ordinary organic solvents, less so in petroleum of high boiling point, containing a little ether, from which it separated in tufts of radiating needles, melting at 46—48°:

Found, $C=43{\cdot}89$; $H=6{\cdot}44$; $OMe=38{\cdot}33$.

$C_4H_4O_3(OMe)_2$ requires $C=44{\cdot}42$; $H=6{\cdot}23$; $OMe=38{\cdot}28$ per cent.

Ten c.c. of an aqueous solution of the acid ester required 12·0 c.c. of standard baryta solution for neutralisation, the calculated quantity being 11·8 c.c.

In aqueous solution, $[\alpha]_D^{20^\circ}$ $-41{\cdot}85^\circ$, $c=6{\cdot}3086$, and $-43{\cdot}28^\circ$, $c=3{\cdot}1543$. In acetone solution, $-60{\cdot}86^\circ$, $c=6{\cdot}9747$, and $-57{\cdot}64^\circ$, $c=3{\cdot}4874$. A weighed portion of the acid ester was exactly neutralised with potassium hydroxide; the specific rotation of the aqueous solution of methyl potassium methoxysuccinate, so obtained, was $[\alpha]_D^{16^\circ}$ −19·05°, $c = 3·936$.

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* All the polarimetric observations recorded in this paper were taken in a 2-dcm. tube.

l-*Methoxysuccinamic Acid.*

Succinimide was first obtained by d'Arcet (*Ann. Chim. Phys.*, 1835, [ii], **58**, 294) by heating succinic anhydride in a current of dry ammonia gas. This process, when applied to methoxysuccinic anhydride, gave a hard, glassy product, soluble in water, which could not be obtained crystalline. When dry ammonia gas was passed into the anhydride at 100°, a pasty, crystalline mass of mixed plates and needles resulted. The former were isolated by repeated crystallisation from methyl alcohol, and finally from a mixture of ethyl alcohol and ether, and proved to be methoxysuccinamic acid (m. p. 144°); the needles were apparently the ammonium salt of this acid. In other similarly conducted experiments, the acid alone was produced. The compound was readily soluble in methyl and ethyl alcohol, also in acetone, slightly so in ether, insoluble in benzene, chloroform, carbon tetrachloride, or ethyl acetate:

Found, C = 40·64; H = 6·35; N = 9·64; OMe = 19·91.

$C_4H_6O_3N(OMe)$ requires C = 40·78; H = 6·18; N = 9·54; OMe = 21·09 per cent.

In aqueous solution, $[\alpha]_D^{20^\circ}$ −29·41°, $c = 4·7777$, and in methyl-alcoholic solution, −46·75°, $c = 3·251$.

Distillation of the acid gave a crystalline product (m. p. 59—61°) having an acid reaction; it evolved ammonia on being heated with potassium hydroxide solution, and approximated in composition to methoxysuccinimide. The substance will be further examined.

d-*Dimethoxysuccinyl Chloride.*

The material used in this and the following preparations was procured by methylation of methyl tartrate and conversion of the resulting methyl dimethoxysuccinate into the corresponding acid through decomposition of the barium salt (Trans., 1901, **79**, 957). The melting point found for methyl dimethoxysuccinate was two degrees higher than formerly recorded (*loc. cit.*), namely, 52—53°. The rotatory power of the ester in benzene solution was identical with that previously given (solvent: acetone, $c = 5·4183$, $[\alpha]_D^{20^\circ}$ 79·63°). An attempt to prepare the acid chloride from the ester by the direct action of phosphorus pentachloride having proved unsuccessful, the dry acid, partly dissolved in benzene, was treated with this reagent in slight excess of the calculated quantity. The reaction having been completed by heating the mixture for some time on a water-bath, the benzene was distilled off. By washing the solid residue with petroleum of high boiling point, and crystallising it from anhydrous ether, the acid chloride was obtained in long, slender prisms, melting at 90—93°. The yield of crystallised chloride from 27·5 grams of acid was 18 grams:

Found, C = 33·19; H = 3·94; Cl = 32·29.
$C_6H_8O_4Cl_2$ requires C = 33·49; H = 3·76; Cl = 32·98 per cent.

The analytical figures showed that the methoxyl groups had not been attacked by the phosphorus pentachloride. This was confirmed by the reproduction of the initial crystalline methyl dimethoxysuccinate when the chloride was treated with methyl alcohol. With water, the chloride gave crystalline dimethoxysuccinic acid. The specific rotation of the chloride in acetone solution is $[\alpha]_D^{20°}$ 79·85°, $c = 5·3913$; in chloroform, 56·87°, $c = 1·2484$; in benzene, 104·14°, $c = 2·0357$.

d-*Dimethoxysuccinic Anhydride.*

This compound was readily obtained in well-defined, apparently cubical crystals (m. p. 80—82°) by heating the acid with four times its weight of acetyl chloride, distilling off the excess of the reagent under diminished pressure, and recrystallising the residual product from chloroform and finally from anhydrous ether. Nine grams of acid gave 7 grams of recrystallised anhydride. The previously recorded failure to obtain the compound by this method (Trans., 1901, **79**, 960) was doubtless due to the action of water contained in the solvent ether. The dry barium salt, obtained by hydrolysis of the methyl ester, may be substituted with advantage for the acid in the above preparation:

Found, C = 44·68; H = 5·19; OMe = 38·87.
$C_4H_2O_3(OMe)_2$ requires C = 44·98; H = 5·05; OMe = 38·77 per cent.

In acetone solution, $[\alpha]_D^{20°}$ 148·7°, $c = 5·2573$, and 148·4°, $c = 2·3148$. By adding a little water to the acetone solution, heating for some time, and evaporating, the crystalline acid was reproduced.

Methyl Hydrogen d-*Dimethoxysuccinate.*

On distilling the product obtained by boiling a methyl-alcoholic solution of the anhydride, a viscous, acid syrup was collected (b. p. 137—142°/16 mm.), which analysis showed to be the above compound. Owing to the viscid nature of the product, the separation of the distilled fractions was imperfect, and the substance was probably not pure: *

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* In a later preparation, the undistilled product was obtained crystalline, but it was found to be contaminated with dimethoxysuccinic acid.

Found, C = 43·73; H = 6·27.

$C_7H_{12}O_6$ requires C = 43·72; H = 6·31 per cent.

In acetone solution, $[\alpha]_D^{20°}$ 91·22°, c = 4·615; in aqueous solution, 69·35°, c = 4·823.

Action of Sodium Methoxide on Methyl l-*Methoxysuccinate.*

A mixture of the ester (1 mol.) and sodium methoxide (2 mols.) in methyl-alcoholic solution was heated at 60° for four hours. On evaporating off the alcohol and pouring the residual oil into ice-cold sulphuric acid, a pale yellow, flocculent solid was precipitated, which was collected and dried on a porous plate in a vacuum desiccator. In a series of experiments under varying conditions, the weight of solid product amounted to only about a tenth of the weight of ester used. For analysis, the substance was precipitated by adding petroleum of high boiling point to its solution in benzene, and dried in a vacuum:

Found, C = 51·31; H = 4·71; OMe = 33·81.

$C_8H_3O_4(OMe)_3$ requires C = 51·54; H = 4·73; OMe = 36·35 per cent.

The low result found for methoxyl is probably accounted for by the incomplete action of the hydriodic acid, due to resinification of the substance. The composition therefore is that of a compound produced by the condensation of 2 molecules of methyl methoxysuccinate with the loss of 3 molecules of methyl alcohol.

Action of Magnesium Methyl Iodide on Methyl d-*Dimethoxysuccinate.*

Twenty grams (1 mol.) of the ester in ethereal solution were added slowly to the ice-cold ethereal solution of the Grignard reagent, prepared from 10·5 grams ($4\frac{1}{4}$ atoms) of magnesium and 62 grams ($4\frac{1}{4}$ mols.) of methyl iodide. The product was boiled for one hour, and then decomposed in the usual manner. The crude product was crystallised from light petroleum. Nine grams of *γδ-dimethoxy-βε-dimethylhexane-βε-diol*, melting at 71°, were obtained:

Found, C = 58·43; H = 10·66; OMe = 31·76.

$C_8H_{16}O_2(OMe)_2$ requires C = 58·19; H = 10·77; OMe = 30·09 per cent.

It crystallises in needles, and is very slightly soluble in water, soluble in alcohol, ether, or benzene, less so in light petroleum. In methyl-alcoholic solution, $[\alpha]_D^{20°}$ −30·9°, c = 3·5244; and in acetone solution, −41·96°, c = 5·0884.

Attempts to acylate and to methylate the compound were not successful. Benzoyl chloride had no action on it, whether applied by the Schotten-Baumann method, or by heating in ethereal solution in the presence of dry sodium carbonate. The process of methylation by means of dry silver oxide and methyl iodide, carried out in the usual manner, with a large excess of alkylating agent, gave a liquid distillate. Estimations of methoxyl in different fractions of this product gave 39·3, 39·4, and 40·9 per cent., which seemed to show that one of the hydroxyl groups of the glycol had been methylated, the figure calculated on this assumption being 42·3 per cent. In view, however, of the very indefinite boiling point of the liquid, we conclude that methylation had in reality only occurred to a slight extent, and that the increase of methoxyl content, shown by the figures quoted, was mainly due to the unmethylated glycol being dehydrated in the course of the distillation.

Dehydrating agents having failed to give a crystalline anhydride, the glycol was subjected to distillation under the ordinary pressure. When rapidly heated, the compound distilled largely unchanged, but when heated slowly, water was given off, and, after repeated distillations, the crystalline matter disappeared and a colourless oil of camphor-like odour was collected (b. p. 181—186°). The following analysis agrees with the supposition that the oil was a mixture of an anhydride, produced by the loss of 1 molecule of water, with about 19 per cent. of unaltered glycol.

Found, $C=62·74$; $H=10·70$.

$C_{10}H_{20}O_3$ requires $C=63·76$; $H=10·73$.

The composition of the mixture was not affected by further distillation. An acetone solution gave $[\alpha]_D^{20}$ 13·35°, $c=4·495$. The anhydride therefore, in contradistinction to the parent glycol, is dextrorotatory. On heating the acetone solution with an equal bulk of water in a sealed tube at 105°, the rotatory power underwent no change, and the anhydride therefore, as was to be expected, is not readily reconverted into the glycol.

Action of Magnesium Phenyl Bromide on Methyl d-*Dimethoxysuccinate: Preparation of* 3 : 4-*Dimethoxy*-2 : 2 : 5 : 5-*tetraphenyltetrahydrofuran.*

When the ester (1 mol.) dissolved in ether was added to an ethereal solution of the Grignard reagent (4 mols.), and the mixture, after being heated for some time, was treated as usual with dilute sulphuric acid, no crystalline substance was isolated from the product. In the following experiment, other conditions being the same, the proportion of the Grignard reagent was increased to 6 molecules, and the mixture was kept overnight without heating. On mixing the ethereal solutions, a considerable action took place, and two layers were formed. The product having been treated in the usual manner, the separated ethereal layer gave, on evaporation, a syrup, which crystallised immediately. The crystalline matter, freed from adhering oil by draining on a porous plate and washing with cold methyl alcohol, amounted to 16 grams. The substance crystallised from ethyl alcohol in beautiful iridescent leaflets, but the indefinite melting point of the recrystallised material, 162—180°, showed that it was impure. By further recrystallisation from petroleum of high boiling point, the melting point was raised to 184—186°:

Found, $C=82{\cdot}79$; $H=6{\cdot}65$.

$C_{30}H_{28}O_3$ requires $C=82{\cdot}51$; $H=6{\cdot}33$ per cent.

Finally, by dissolving in benzene and adding ether, a crop of crystals (8 grams) was deposited in flat prisms. When these were heated at 120—130°, they became powdery, probably from escape of adhering solvent, and then melted sharply at 184—185°.* (Found, $C=82{\cdot}06$; $H=6{\cdot}63$.) On distilling in a current of steam, no diphenyl could be detected.

The substance was saturated, as it was not attacked after remaining twelve hours in a carbon disulphide solution of bromine.

In attempting to estimate methoxyl in the usual way, no action was perceptible, and after the process the substance was recovered unchanged. Even in the presence of acetic anhydride resinification occurred, and the action of the hydriodic acid was very incomplete. By heating the substance with a mixture of acetic anhydride and hydriodic acid in a sealed tube at 200°, and completing the analysis in the usual apparatus according to Zeisel's method, a result approximating to the calculated figure was obtained:

Found, $OMe=12{\cdot}87$.

$C_{28}H_{22}O(OMe)_2$ requires $OMe=14{\cdot}22$ per cent.

The compound is insoluble in water and in aqueous alkali, moderately soluble in hot alcohol, more so in acetone and in warm light petroleum, and very soluble in chloroform or benzene. In benzene solution, $[\alpha]_D^{20^\circ}$ $-115{\cdot}7^\circ$, $c=8{\cdot}272$.

We wish to thank Miss M. A. Dunbar for assistance given in part of the experimental work.

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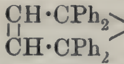
* From further experiments, we have reason to believe that the true melting point is considerably higher than is recorded, and that the crude product (m. p. 162—180°) contained a compound of lower melting point, which was not isolated.

CXLII.—*Action of Grignard Reagents on Methyl* l-*Methoxysuccinate, Methyl Maleate, and Maleic Anhydride.*

By THOMAS PURDIE, F.R.S., and PAUL SEIDELIN ARUP, B.Sc.

IT has been shown in the preceding paper that magnesium methyl iodide and magnesium phenyl bromide act on methyl *d*-dimethoxysuccinate in the same manner as on unsubstituted succinic esters. Magnesium methyl iodide gives $\gamma\delta$-dimethoxy-$\beta\epsilon$-dimethylhexane-$\beta\epsilon$-diol, and the phenyl bromide yields 3 : 4-dimethoxy-2 : 2 : 5 : 5-tetraphenyltetrahydrofuran. The etheric methoxyl groups are not attacked in either case, and the products are therefore optically active.

We find that the action of magnesium methyl iodide on methyl *l*-methoxysuccinate is similar to that of the same reagent on the dimethoxy-ester, the product being optically active γ-methoxy-$\beta\epsilon$-dimethylhexane-$\beta\epsilon$-diol, $HO\cdot CMe_2\cdot CH(OMe)\cdot CH_2\cdot CMe_2\cdot OH$. The glycol, however, could not be obtained in the pure state. The product, being a liquid, was isolated by distillation in a vacuum, and this caused partial dehydration. By distillation under atmospheric pressure, complete dehydration was effected, and the final product obtained was the oxide of the glycol (a furan derivative), or possibly an isomeric unsaturated alcohol. In acetone solution, the compound gave $[\alpha]_D + 44\cdot 9°$. Calculating the rotatory power of the glycol in acetone solution from that of a mixture with the anhydride, the approximate composition of which was determined by the results of analysis, the value should be about $[\alpha]_D + 35°$. The initial ester being lævorotatory, the conversion of ester into glycol results in a change of sign of rotation. This is also the case in the production of the corresponding dimethoxy-glycol from the dimethoxy-ester (see the preceding paper). But whilst the conversion of the latter glycol into its oxide brings about a second reversal of the sign, in the dehydration of the mono-methoxy-glycol the sign remains the same. This difference is not in agreement with the usual optical effect of ring formation, and suggests that the dehydration referred to above proceeds on different lines, giving possibly an unsaturated alcohol.

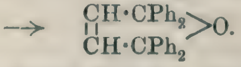
The action of magnesium phenyl bromide on methyl *l*-methoxysuccinate proved to be more complex than that of magnesium methyl iodide. Two crystalline compounds were isolated from the product of the reaction, having respectively the composition $C_{23}H_{22}O$ (m. p. 190—191°) and $C_{22}H_{18}O_2$ (m. p. 160—161°), but neither contained methoxyl, and both were optically inactive. The former substance was found to be 2:2:5:5-tetraphenyl-2:5-dihydrofuran,  $\left.\begin{array}{l}\mathrm{CH\cdot CPh_2}\\ \|\\ \mathrm{CH\cdot CPh_2}\end{array}\right>\mathrm{O}$, and the latter a triphenylbutyrolactone.

The unsaturated character of the dihydrofuran derivative was exhibited in its behaviour towards bromine, with which it readily combined, and by its rapidly decolorising cold alkaline permanganate solution. The constitution was deduced from the following observations. Oxidation by boiling dilute alkaline permanganate solutions gave benzophenone. Distillation with zinc dust, according to Baeyer's process, gave a hydrocarbon, $C_{28}H_{20}$ (m. p. 157—158°), and reduction of this with sodium and amyl alcohol gave the *αα*δδ-tetraphenylbutane, $\mathrm{CHPh_2\cdot CH_2\cdot CH_2\cdot CHPh_2}$, which Valeur (*Bull. Soc. chim.*, 1903, [iii], **29**, 683) obtained similarly from tetraphenylbutadiene, $\mathrm{CPh_2\colon CH\cdot CH\colon CPh_2}$. The hydrocarbon $C_{28}H_{20}$ agrees in melting point and composition with a hydrocarbon obtained by Buttenberg (*Annalen*, 1894, **279**, 329) from the action of concentrated sulphuric acid on ββ-diphenylvinyl ether, $\mathrm{CPh_2\colon CH\cdot OEt}$, and the substances are presumably identical. The only formula for the hydrocarbon, consistent with the result of its reduction, as given above, with the molecular weight found by us, and with Buttenberg's method of preparation, appears to be $\mathrm{CPh_2\colon C\colon C\colon CPh_2}$.

The constitution of the dihydrofuran derivative suggested that the disappearance of the methoxyl group was due to the abstraction of a molecule of methyl alcohol from the monomethoxysuccinate with the production of a maleic or fumaric ester or other derivative, which was then further acted on by the Grignard reagent. We accordingly examined the action of magnesium phenyl bromide on methyl fumarate and maleate and on maleic anhydride.

Methyl fumarate gave an uncrystallisable syrup, the examination of which yielded no definite result. Methyl maleate, however, gave the same tetraphenyldihydrofuran which has been already described. The reaction is of a normal kind, and may be thus represented:

$$\mathrm{CO_2Me\cdot CH\colon CH\cdot CO_2Me} \longrightarrow \mathrm{BrMgO\cdot CPh_2\cdot CH\colon CH\cdot CPh_2\cdot OMgBr}$$

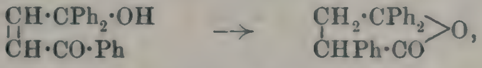


$$\longrightarrow \left.\begin{array}{l}\mathrm{CH\cdot CPh_2}\\ \|\\ \mathrm{CH\cdot CPh_2}\end{array}\right>\mathrm{O}.$$

It appears therefore that in the case of methyl methoxysuccinate, methyl alcohol is split off from the ester at the outset, or at an early stage, of the Grignard reaction, which otherwise follows the normal course. The second product of the action of magnesium phenyl bromide on methyl methoxysuccinate has been already referred to as triphenylbutyrolactone (m. p. 160—161°); we assign a lactonic structure to the compound on the following grounds.

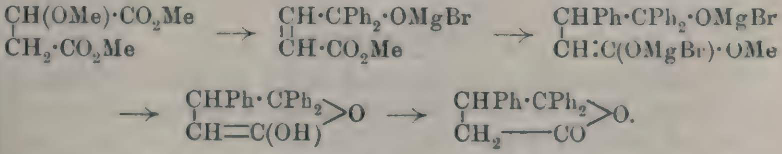
The substance showed neither alcoholic nor ketonic properties, and it behaved as a saturated compound. It dissolved sparingly, and only on prolonged boiling, in aqueous potassium hydroxide and ammonia solutions. It was, however, converted by boiling alcoholic potash into a potassium salt, which, after removal of the alcohol, dissolved completely in water. The aqueous solution of the salt gave with mineral acids a white, flocculent precipitate, which was soluble with effervescence in cold sodium carbonate solution, and was doubtless hydroxytriphenylbutyric acid. The precipitated acid, after being dried at 90°, melted at 140—145°, and still decomposed warm sodium carbonate solution, but after being heated for an hour at 130°, it was no longer soluble in sodium carbonate, and then showed the melting point of the original substance, 160°.

With respect to the position of the three phenyl groups, we regard the compound provisionally as $\beta\gamma\gamma$-triphenylbutyrolactone, for the following reasons. As the substance gives benzophenone on oxidation, two of the phenyl groups must be attached to the same carbon atom, and without assumption of improbable transposition, this can only be the γ-carbon atom. The phenyl groups must therefore be in the $\alpha\gamma\gamma$-or $\beta\gamma\gamma$-positions. The former constitution implies a transposition of the following kind:



$$\begin{array}{l}\mathrm{CH\cdot CPh_2\cdot OH}\\ \mathrm{CH\cdot CO\cdot Ph}\end{array} \longrightarrow \begin{array}{l}\mathrm{CH_2\cdot CPh_2}\\ \mathrm{CHPh\cdot CO}\end{array}\!\!>\mathrm{O},$$

which is certainly not improbable. A $\beta\gamma\gamma$-lactone, however, might result normally from the Grignard reaction according to the following scheme:



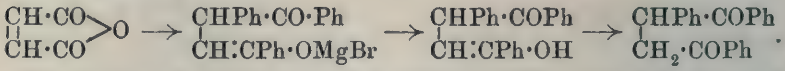
$$\begin{array}{l}\mathrm{CH(OMe)\cdot CO_2Me}\\ \mathrm{CH_2\cdot CO_2Me}\end{array} \longrightarrow \begin{array}{l}\mathrm{CH\cdot CPh_2\cdot OMgBr}\\ \mathrm{CH\cdot CO_2Me}\end{array} \longrightarrow \begin{array}{l}\mathrm{CHPh\cdot CPh_2\cdot OMgBr}\\ \mathrm{CH{:}C(OMgBr)\cdot OMe}\end{array}$$

$$\longrightarrow \begin{array}{l}\mathrm{CHPh\cdot CPh_2}\\ \mathrm{CH{=}C(OH)}\end{array}\!\!>\mathrm{O} \longrightarrow \begin{array}{l}\mathrm{CHPh\cdot CPh_2}\\ \mathrm{CH_2{-\!\!-}CO}\end{array}\!\!>\mathrm{O}.$$

The addition of the Grignard reagent is here supposed to take effect in the 1 : 4-position, which Kohler has found to be a common mode of action with unsaturated ketones and esters (*Amer. Chem. J.*, 1904, **31**, 642, etc.).* We failed to obtain evidence of this mode of addition in the case of methyl maleate, but we find, on the other hand, that maleic anhydride reacts with magnesium phenyl bromide, probably in the manner in question, the product being A. Smith's

* If direct addition of the Grignard reagent to the two unsaturated carbon atoms occurs, then either an $\alpha\gamma\gamma$- or $\beta\gamma\gamma$-lactone might be formed. The action is, in other respects, like that described by Shibata in the case of the phthalic esters (Trans., 1909, **95**, 1449).

desylacetophenone (Trans., 1890, **57**, 643). The action may be formulated thus:



$$\begin{array}{l}\mathrm{CH\cdot CO}\\ \|\\ \mathrm{CH\cdot CO}\end{array}\!>\mathrm{O} \longrightarrow \begin{array}{l}\mathrm{CHPh\cdot CO\cdot Ph}\\ |\\ \mathrm{CH{:}CPh\cdot OMgBr}\end{array} \longrightarrow \begin{array}{l}\mathrm{CHPh\cdot COPh}\\ |\\ \mathrm{CH{:}CPh\cdot OH}\end{array} \longrightarrow \begin{array}{l}\mathrm{CHPh\cdot COPh}\\ |\\ \mathrm{CH_2\cdot COPh}\end{array}.$$

The triphenylbutyrolactone (m. p. 160—161°) sublimes unchanged when heated alone under diminished pressure, but when heated with mineral acids it is converted nearly quantitatively into an isomeric lactone, melting at 197°. The latter substance resembled the former in giving benzophenone on oxidation, in its behaviour as a saturated compound, and in its insolubility in cold alkali hydroxide solutions. It dissolved, however, much more readily than the former lactone in boiling aqueous potassium hydroxide and ammonia solutions, and the acid which was precipitated on acidification—presumably a triphenylhydroxybutyric acid—lost its solubility in sodium carbonate, and regained the original melting point, 197°, on being simply dried in a vacuum without heating. The solution of the potassium salt coagulated to a jelly on cooling, which redissolved on sufficient water being added. A silver salt of the corresponding hydroxy-acid was precipitated on adding silver nitrate to an ammonia solution of the lactone after the excess of ammonia had been boiled off. After being dried at 100°, it gave $\mathrm{Ag}=24{\cdot}87$; $C_{22}H_{19}O_3Ag$ requires $\mathrm{Ag}=24{\cdot}59$ per cent. The production of the lactone just described might be accounted for by the migration of a phenyl group, but we refrain from discussing the nature of the isomeric change until the two lactones and the acids derivable from them have been further examined.

EXPERIMENTAL.

The methyl *l*-methoxysuccinate used in the following experiments was obtained by methylating methyl malate by means of dry silver oxide and methyl iodide.

The boiling point of the liquid ester was 135°/42 mm., and it gave $[\alpha]_D^{15^\circ}\ -54{\cdot}2^\circ$.

Action of Magnesium Methyl Iodide on Methyl l-*Methoxysuccinate.*

Preliminary experiments showed that the product of the action was an uncrystallisable oil. Using four molecular proportions of the Grignard reagent to one of the ester, the carbon content of the distilled product indicated that the action was incomplete, but with excess of the reagent, a liquid of lower boiling point was obtained having approximately the composition of an anhydride of the ditertiary glycol, which was expected to result from the reaction. In the following experiment, therefore, an excess of the Grignard reagent was employed.

Ten grams of the ester (1 mol.), dissolved in ether, were added slowly to an ethereal solution of magnesium methyl iodide, prepared from 10 grams (7·4 atoms) of magnesium. After the brisk reaction which ensued had subsided, the mixture was heated for three hours on a water-bath, and thereafter decomposed in the usual way with dilute sulphuric acid. The product was then thoroughly extracted with ether. The dried ethereal solution gave, on evaporation, a brownish oil, which was distilled under diminished pressure. Some water was produced during the distillation, presumablv from decomposition of the glycol, and 10 grams of a colourless, mobile liquid, with a camphoraceous odour, were collected at 60—90°/90 mm. After distilling this twice, a fraction (b. p. 63—64°/33 mm.), weighing 4·5 grams, was obtained, which gave, in acetone solution, $[\alpha]_D^{20^\circ}$ +42·5° ($c=2·2336$), and on analysis C = 66·75, H = 11·36, OMe = 19·3. The expected ditertiary glycol, $C_8H_{17}O_2(OMe)$, requires C = 61·36, H = 11·36, OMe = 17·61 per cent.; its anhydride, $C_{18}H_{15}O(OMe)$, requires C = 68·35, H = 11·39, OMe = 19·62 per cent.

The liquid was presumably a mixture of the ditertiary glycol and its oxide, the latter having been produced by the elimination of water in the course of the distillation. As it was found that but little increase of the carbon content was brought about by further distillation under diminished pressure, the liquid was now distilled under the atmospheric pressure. A fraction collected after two distillations (b. p. 150—151°) gave C = 67·88, H = 11·39, OMe = 19·17.

The substance is therefore a dehydration product of the glycol, γ-methoxy-βε-dimethylhexane-βε-diol. A cryoscopic determination of the molecular weight in benzene solution gave 152; $C_8H_{15}O(OMe)$ requires 158. The specific rotation in acetone solution was $[\alpha]_D^{20^\circ}$ 44·9°, $c=3·9185$, $l=2$.

Action of Magnesium Phenyl Bromide on Methyl l-*Methoxysuccinate.*

The conditions observed in the following experiment were found to be the most advantageous in respect of the yield of crystalline product. Thirty grams of the ester (1 mol.) in ethereal solution were added slowly to an ethereal solution of the Grignard reagent prepared from 33 grams of magnesium (8 atoms) and 215 grams of bromobenzene (8 mols.) A vigorous reaction occurred. After remaining twelve hours at the ordinary temperature, the mixture was treated with ice-cold dilute sulphuric acid in the usual manner. On evaporating the ethereal layer, successive crops of crystals were deposited, in all 44 grams, which were found to consist of two substances melting at 190—191° and 160—161° respectively. The separation of these was effected by dissolving each of the crops in benzene and adding one and a-half times as much ether to each solution. This treatment precipitated the much less soluble compound of higher melting point, and, on concentrating the mother liquors, the compound melting at the lower temperature was deposited. By systematic repetition of the process, 7·5 grams of each substance were obtained nearly pure; the remaining material consisted mostly of the compound (m. p. 160—161°), which was the main crystalline product of the reaction.

As already stated, the compound melting at 190—191° is 2 : 2 : 5 : 5-tetraphenyl-2 : 5-dihydrofuran, and the compound melting at 160—161° a triphenylbutyrolactone.

2 : 2 : 5 : 5-*Tetraphenyl*-2 : 5-*dihydrofuran* crystallises from a mixture of benzene and ether in fine needles. It is moderately soluble in cold benzene, sparingly so in cold alcohol, acetone, or petroleum of high boiling point, but fairly soluble in the hot solvents, and almost insoluble in boiling ether. It crystallises unchanged from hot glacial acetic acid:

Found, $C=89·56$; $H=6·00$.

$C_{28}H_{22}O$ requires $C=89·84$; $H=5·88$ per cent.

The following observations are in accord with the constitution assigned to the compound. A 6 per cent. solution in benzene at 40° was optically inactive. On applying Zeisel's process for estimating methoxyl to a solution of the substance in acetic anhydride, no silver iodide was formed, even when the temperature was raised to 130°. An alcoholic solution of the compound reduced alkaline permanganate instantly in the cold. On adding bromine (2 atoms) in carbon disulphide solution to the compound (1 mol.) in the same solvent, an additive compound was evidently formed, as the colour of the bromine disappeared quickly in the dark, and a crop of yellow, acicular crystals was deposited. On attempting to recrystallise the substance, however, decomposition occurred with liberation of hydrogen bromide, and estimation of bromine in different preparations gave varying figures approximating to those required for a monobromo-derivative.

Oxidation of the furan derivative with a boiling dilute alkaline solution of potassium permanganate gave benzophenone. The product was isolated by distillation in a current of steam, and was identified by its melting point (48°), and by that of the phenylhydrazone prepared from it (136°).

The reduction of the compound was effected by distilling 9·5 grams with zinc dust in a current of hydrogen at a temperature considerably below a red heat. The distillate solidified, on cooling, to an amber-coloured glass, which was deposited in a crystalline state from a solution in a mixture of ethyl alcohol and ether. After three crystallisations from this medium, 2·4 grams of colourless, rectangular plates were obtained, melting at 157—158°. The substance was sparingly soluble in alcohol, readily so in ether, benzene, or chloroform, and decolorised cold alkaline permanganate instantly:

Found, (I) C=93·85; H=5·80. (II) C=94·17; H=5·94.

$C_{28}H_{20}$ requires C=94·38; H=5·62 per cent.

The molecular weight in chloroform solution, determined by the ebullioscopic method, was 364. $C_{28}H_{20}$ requires 356.

One gram of the hydrocarbon was dissolved in 50 c.c. of boiling amyl alcohol, and 10 grams of sodium were added in small pieces. The hot solution was then poured into a mixture of 400 c.c. of water and 7 grams of glacial acetic acid. The alcoholic layer, evaporated under diminished pressure to half its bulk, gave 0·4 gram of crystalline, rectangular plates, which, after being recrystallised from ethyl alcohol, melted at 121°. The substance resembled stilbene, but it was found that admixture with pure stilbene caused a considerable lowering of the melting point, and, moreover, it decolorised cold dilute alkaline permanganate only after some time. (Found, C=92·47; H=6·93. Calc., C=92·82; H=7·18 per cent.) This hydrocarbon, as already stated, is **ααδδ**-tetraphenylbutane.

Triphenylbutyrolactone (m. p. 160—161°), which was isolated, as already described, from the crude product of the action of the Grignard reagent, crystallises in microscopic needles. It is readily soluble in cold acetone or chloroform, moderately so in cold ether, sparingly so in cold alcohol and benzene, but fairly soluble in the latter solvents when hot. At 200°/20 mm. it sublimes unchanged in beautiful prisms:

Found, (I) C=83·85; H=6·01. (II) C=83·91; H=5·98.

$C_{22}H_{18}O_2$ requires C=84·08; H=5·73 per cent.

The molecular weight in chloroform solution, determined by the ebullioscopic method, was 337. $C_{22}H_{18}O_2$ requires 314.

The compound was optically inactive. Only a trace of silver iodide was formed when 2 grams of it were heated with hydriodic acid for one and a-half hours according to Zeisel's process. It was not affected by heating with an alcoholic solution of hydroxylamine for nine hours at 160°, by boiling for three hours with acetyl chloride, or by shaking with benzoyl chloride and sodium hydroxide solution. In each case, the substance was recovered unchanged after the treatment. It decolorised an alkaline solution of potassium permanganate in the cold only slowly, and it was recovered unaltered after being twelve hours in contact with bromine in carbon disulphide solution. Oxidation with boiling dilute alkaline permanganate solution gave benzophenone, which was identified by conversion into the oxime. The lactonic behaviour of the compound has been already described.

Action of Mineral Acids on Triphenylbutyrolactone (m. p. 160—161°).

In testing for methoxyl by Zeisel's method in an impure fraction obtained by crystallising the crude product of the Grignard reagent, 2 grams of the material, melting about 140°, were boiled with hydriodic acid (D 1·7) for one and a-half hours. The residual solid from this treatment, after being washed with water and a little alcohol, and recrystallised from benzene, weighed 1·6 grams, and now melted at 192—196°. Similar treatment of the pure triphenyllactone (m. p. 160—161°) showed that the change of melting point was due to the apparently quantitative conversion of this compound into an isomeric lactone, melting at 197°. The same change occurred when the lactone of lower melting point was heated with concentrated hydrochloric acid in a sealed tube, or with sulphuric acid (70 per cent. by volume) for two hours at 140°.

Triphenylbutyrolactone (m. p. 197°) crystallises from chloroform or benzene in well-defined, prismatic needles. It is insoluble in water, moderately soluble in cold ether and acetone and in hot benzene, readily so in hot chloroform, but sparingly soluble in the two latter solvents or alcohol when cold. The compound proved to be optically inactive:

Found, (I) C = 84·22; H = 5·89. (II) C = 84·10; H = 5·81.

$C_{22}H_{18}O_2$ requires C = 84·08; H = 5·73 per cent.

By oxidation with boiling dilute alkaline permanganate solution, 1 gram of the substance gave 0·4 gram, nearly the calculated yield, of benzophenone (m. p. 47—49°). Baeyer's permanganate test showed that the compound was saturated, and this was confirmed by its resistance to a cold solution of bromine in carbon disulphide. After being in the bromine solution for twelve hours, the compound was recovered unchanged. The lactonic properties of the substance have been already described in the introduction.

Action of Magnesium Phenyl Bromide on Methyl Maleate.

Methyl maleate was prepared by the interaction of methyl iodide and silver maleate, the latter being obtained from maleic anhydride. Twenty grams of the anhydride gave 23 grams of the ester (b. p. 201—205°).

Ten grams of methyl maleate (1 mol.) were treated with magnesium phenyl bromide obtained from 6·7 grams of magnesium

(4 atoms) and 44 grams of bromobenzene (4 mols.). The procedure was the same as in the previous cases. After the spontaneous vigorous action had subsided, the mixture was heated for an hour on the water-bath, and then treated in the usual manner. The ethereal layer, on evaporation, left a syrup which deposited crystalline matter after some time. The syrup having been removed by stirring the product with a little ether, 2 grams of residual solid were collected and recrystallised by dissolving it in benzene and adding ether. By repeating the process, 1·2 grams of pure substance were obtained in fine, colourless needles, which melted sharply at 190°. The solubilities of the compound, the melting point, and the results of analysis showed it to be the same 2 : 2 : 5 : 5-tetraphenyl-2 : 5-dihydrofuran already described as one of the products of the action of the Grignard reagent on methyl methoxysuccinate. (Found, C = 89·41 ; H = 6·14. Calc., C = 89·84 ; H = 5·88 per cent.)

The syrup which constituted the main product of the reaction was distilled under diminished pressure, but diphenyl was the only crystalline substance found in it. The syrup was boiled with hydriodic acid in the hope that the lactone (m. p. 197°) might be produced, but without result.

Action of Magnesium Phenyl Bromide on Maleic Anhydride.

The method pursued was the same as in the action with methyl maleate. The materials were 10 grams of maleic anhydride (1 mol.) and magnesium phenyl bromide prepared from 11 grams of magnesium (4·5 atoms) and 72 grams of bromobenzene (4·5 molecules). The reaction was vigorous, and was moderated by cooling in ice. The mixture was heated for an hour after spontaneous action had ceased, and was then treated in the usual manner. The oil, left on evaporating the ethereal extract, soon deposited crystalline matter, which was collected and washed with a little alcohol. The total isolated product consisted of 10 grams of nearly pure crystalline substance, and about an equal weight of uncrystallisable oil. The crystals, after being once recrystallised from alcohol containing a few drops of acetic acid and once from absolute alcohol, melted sharply at 126—127°. (Found, C = 84·16 ; H = 5·93. $C_{22}H_{18}O_2$ requires C = 84·08 ; H = 5·73 per cent.)

The substance was therefore isomeric with the two lactones previously described, but its insolubility in potassium hydroxide solution on long boiling showed that its character was neither acidic nor lactonic. It proved to be identical with A. Smith's desylacetophenone (Trans., 1890, **57**, 643) ($\alpha\delta$-diketo-$\alpha\beta\delta$-triphenylbutane), which he found to be converted into 2 : 4 : 5-triphenylfuran (m. p. 92°) by cold concentrated sulphuric acid. On following Smith's directions, we obtained from our product by the action of sulphuric acid a crop of acicular crystals which melted at 92°, and otherwise resembled the furan derivative referred to. The identity was confirmed by analysis. (Found, C=88·85; H=5·62. Calc., C=89·19; H=5·41 per cent.)

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CXLIII.—*The Absorption Spectra of Aniline and its Homologues as Vapours, as Liquids, and in Solution.*

By JOHN EDWARD PURVIS.

THE aim of this communication is to give an account of a comparative study of the absorption spectra of aniline and its liquid homologues, in the state of vapours, liquids, and in solution, in order to ascertain, under these conditions, (1) the nature of the influence on the absorption of the radiant energy, and (2) how far the replacement of the hydrogen atoms by simple groups in the nucleus, or in the side-chain, affects the extent and type of the absorption bands.

The substances examined were aniline, mono- and di-methylaniline, mono- and di-ethylaniline, *o*- and *m*-toluidine, *o*-3-xylidine, *m*-2-xylidine, mesidine, and benzylamine. The substances were distilled several times before use.

EXPERIMENTAL.

Vapours.

The absorption spectrum of the vapour of aniline in a tube 1-dcm. long, and at 35°, has been studied by Pauer (*Wied. Ann.*, 1897, **61**, 374), who measured the positions of sixteen absorption bands, employing the radiant energy of the Cd spark. More recently, Grebe (*Diss.*, Bonn, 1905; and *Zeitsch. wiss. Photochem.*, 1905, **3**, 363) studied the vapour of aniline at 25—30°, and used the continuous spectrum obtained when a powerful spark was passed between aluminium poles immersed in water. He noted the presence, and measured the positions of twenty-eight bands. Neither of these observers, however, investigated the effect of varying the temperature and pressure.

The author has already given an account of the absorption spectra of the vapours of pyridine and some of its derivatives (this vol., pp. 692 and 1035), and the apparatus used in this investigation is described in the first cited paper. Each band was separately measured at the different temperatures and pressures, and on the more refrangible edge.

Aniline.

TABLE I.

The absorption bands in aniline vapour at various temperatures and pressures in a column 2-dcm. long. Barometric pressure = 763 mm.

Abbreviations: w. = weak; mod. str. = moderately strong; str. = strong; v.w. = very weak; r.w. = rather wide; narr. = narrow; mod. w. = moderately weak; v. str. = very strong. The brackets of the wave-lengths represent the measurements of similar related bands; they are not measurements of the width of the bands.

14°. 763 mm. λ.		30°. 807 mm. λ.		45°. 833 mm. λ.	
2978	w.	2978	mod. w.	2981	w., narr.
2977	w.	2977	w.	2978	mod. str., narr.
2975·5	w.	2974·5	mod. str.	2977	w.
2973	w.	2973	mod. w.	2975	str., narr.
2969·5	w.	2970·5	mod. str.	2973	mod. str.
2966·5	mod. str.	2967	,,	2970·5	mod. str., wider
2964	w.	2964	w., r.w.		than 2973
2961·5	mod. str.	2962	mod. str.	2966·5	mod. str.
2958	,, ,,	2959	,,	2963	,,
2953·5	w.	2954·5	w., r.w.	2962	,,
2951	w.	2951·5	w., r.w.	2958·5	,, narr.
2949	w.	2950·5	mod. str., narr.	2954·5	w., wide
2945	mod. str.	2946	,,	2951	,,
2942·5	str.	2943	v. str.	2949	mod. str., narr.
2940	wider and	2940	wider and	2946	,, ,,
	stronger than 2942·5		stronger than 2943	2942·5	str., wide
2935	mod. str.	2934	mod. str.	2939	,, ,,
2931	v.w. equally	2930	w.	2934	str., narr.
2928	v.w. strong	2927·5	w.	2931	w., wide
2923·5	v.w.	2924	w.	2928·5	,,
2921·5	v.w.	2921·5	w., narr.	2924·5	,,
2919	mod. str.	2918	str.	2921·5	w., narr.
2914	str.	2913·5	wider and	2918	str., wide
2912·5	v.w.		stronger than 2918	2913·5	,, ,,
2909	v.w.	2912·5	v.w.	2912	v.w.
2907	v.w.	2910	w., wide	2909·5	w., narr.
2901	mod. str.	2907	w., narrower	2906	w., wide
2897·5	str.		than 2910	2900	,,
2894	v.w.	2900	mod. str., narr.	2897	v.w., wide
2891·5	w.	2897	str.	2893	w.
2879	v.w.	2894	v.w.	2891	mod. str., wide
2877	v.w.	2891	mod. str., narr.	2878·5	v.w.
2875	v.w.	2878·5	w., narr.	2877·5	v.w.
2874	v.w.	2877·5	,,	2876	v.w.
2871	v.w.	2876	,,	2875	v.w.
2870	v.w.	2875	,,	2872	v.w.
2868	w., wide	2872	,,	2871	v.w.
2866	w., wide	2871	,,		
2864	w., narr.	2868	w., wide		
2862	w., narr.	2866	,,		

General absorption began about λ 2850.

36 bands.

14°.
763 mm.

λ.		
2859·5	str., wide	
2857	mod. str.	
2856	w., narr.	
2853·5	v.w.	
2851·5	v.w., narr.	equally strong
2848·5	,, ,,	
2846	,, ,,	
2844	,, ,,	
2841	,, ,,	
2838	,, ,,	
2836	,, ,,	
2834·5	w.	
2832	w.	
2830	mod. w.	equally strong
2828	,,	
2826·5	,,	
2821	head of wide band	
2814·5	v.w.	
2810·5	v.w.	
2807	v.w., stronger than other two	
2804·5	mod. str.	
2798·5	w.	
2794·5	w.	
2791·5	w.	
2787	w., wide	
2782	w., wide	
2781	v.w.	
2779	v.w.	
2770	v.w.	
2768·5	v.w.	
2766	v.w.	
2764·5	v.w.	
2759	v.w.	
2757·5	v.w.	
2755	v.w.	
2739	v.w.	
2737	v.w.	
2729	w.	
2730	mod. str.	
2726	v.w.	
2725	v.w.	
2722	v.w.	
2720·5	v.w., wide	
2717·5	,, ,,	

General absorption began at about λ 2400; Cd lines 2321, 2313, 2288, 2265, 2194, 2144 were just visible.

83 bands.

30°.
807 mm.

λ.	
2864	w., narr.
2862	w., stronger than 2864
2859·5	str., wide
2857	mod. str.
2856	w., narr.
2854·5	,,
2851·5	v.w., narr.
2849	,, ,,
2847	,, ,,
2844·5	v.w., f. wide
2841·5	,, ,,
2838	w., narr.
2836	,,
2834·5	,,
2832·5	,,
2830·5	r.w.
2828	,,
2826·5	,,
2821	head of strong wide band
2816	w., narr.
2812	,,
2808·5	,,
2805	mod. str.
2799	w., r.w.
2795	,,
2791·5	,,
2787	,,
2783	,,
2781	v.w.
2778	v.w., narr.
2770·5	w., narr.
2768·5	,,
2766·5	,,
2765·5	,,
2759·5	mod. str., wide
2757·5	w., narr.
2754	mod. str., narr.
2744	v.w., narr.
2743	,, ,,
2740	w., wide
2737·5	,,
2729	mod. str.
2730	stronger than 2729
2726·5	w., narr.
2725	,,
2723	,,
2720·5	w., wide
2717·5	,,

General absorption began at about λ 2430.

85 bands.

60°.
863 mm.

λ.	
3005	v.w., wide
3000	,, ,,
2995	w., narr.
2993	v.w., narr.
2989	,, ,,
2985	mod. str., wide
2978	,, ,,
2975	,, ,, stronger than 2878
2972	mod. str., wide
2970	,, ,,
2966	,, ,,
2962	,, ,
2958·5	,, ,,

General absorption began at about λ 2940; the Cd line 2948 was just visible.

13 bands.

75°.
893 mm.

λ.	
3005	w., wide
3000	,,
2995	,,
2993	,,
2989	,,
2985	,,

General absorption began at about λ 2980.

6 bands.

90°.
923 mm.
λ.

No bands and general absorption began at about λ 3070.

The absorption spectrum of aniline vapour was also observed at a constant temperature of 17·5° and at gradually diminished pressures. The number and position of the bands were the same as those observed at 14° and 763 mm. pressure in the above table; but they became sharper and weaker as the pressure decreased, and the position of general absorption was shifted towards the more refrangible regions of the spectrum. For example, under 754 mm. pressure the general absorption began at about λ 2400, the Cd lines 2329, 2321, 2313, 2288, 2265, 2194, 2144 were very weak; under 474 mm. pressure the general absorption began at about λ 2390, and the Cd lines beyond were stronger; whilst under 24 mm. pressure the general absorption began at about λ 2370, and the Cd lines were very strong.

The bands are more of the nature of strong lines than of what is usually understood by a band; and the width of many of them is measurable to the same degree and in the same sense as the images of many of the bright lines in emission spectra. They are not nearly so wide as an Ångström unit, and the width of some of the narrow bands is not measurable at all. The constitution and appearance of the bands is completely different from those of the vapour of benzene as described by Hartley (*Phil. Trans.*, 1907, *A*, **208**, 475). Most of the latter appear to be wide bands, sharp and strong on the more refrangible edge.

The results prove that (1) an increase in the temperature and pressure produces a strengthening and widening of the bands, and the appearance of new bands on the less refrangible side; (2) a decrease in the pressure, the temperature remaining constant, produces a weakening and narrowing of the bands. At the same time, (3) an increase in the temperature and pressure produces a shift of the region of general absorption towards the red end; whilst (4) a decrease in the pressure, the temperature remaining constant, produces a shift in the opposite direction.

The bands observed in the vapour of aniline occur chiefly as a series of doublets and triplets; some of them are sharper on the more refrangible edge, whilst others have the edges equally sharp; some of the doublets appear to be equally strong, and some of them show the less refrangible of the two not quite so strong as the more refrangible one. Of the triplets, some have the three constituents equally strong, and of others the most refrangible constituent is the strongest. In addition to these general observations, an attempt has been made to arrange the bands in a definite and regular manner. The following table indicates fairly consistent differences in the wave-lengths of the majority of the bands, considered as a whole:

3005					2985				
35	3000				31	2978			
2970	33	2995			2954	27	2977		
30	2967	31	2993		33	2951	28	2975	
2940	32	2964	31	2989	2921	32	2949	30	2973
33	2935	33	2962	30	42	2919	35	2945	30
2907	34	2931	34	2959	2879	42	2914	33	2943
	2901	34	2928	35	19	2977	39	2912	34
2870	33	2897	34	2924	2860	20	2875	38	2909
21	2868	31	2894	33	24	2857	19	2874	38
2849	21	2866	30	2891	2836	23	2856	20	2871
	2847	22	2864	29	31	2834	24	2854	20
2827	26	2844	23	2862	2805	35	2832	24	2851
45	2821	29	2841	24	39	2799	37	2830	23
2782	40	2815	29	2838	2766	34	2795	38	2828
43	2781		2812	29	41	2765	36	2792	
2739	44		42	2809	2725	43	2759	34	
	2737		2770	40		2722	39	2758	
			40	2769			2720	41	
			2730	43				2717	
				2726					

The numbers run consecutively from left to right and diagonally, and the differences are differences in Ångström units between successive band intervals.

In addition to the regularity observed from comparing the whole of the bands, there are various minor groups which appear to be related. Of these, the following are a series of well-marked doublets whose most refrangible constituent is the strongest:

$$\left.\begin{matrix}2978\cdot0\\2974\cdot5\end{matrix}\right\rangle 3\cdot5 \qquad \left.\begin{matrix}2949\\2945\end{matrix}\right\rangle 4 \qquad \left.\begin{matrix}2918\cdot0\\2913\cdot5\end{matrix}\right\rangle 4\cdot5 \qquad \left.\begin{matrix}2901\\2897\end{matrix}\right\rangle 4$$

or, if the corresponding members of each group are arranged in tabular form, the following differences are observed:

$$\begin{array}{ll}2978 & \\ & \rangle 29 \\ 2949 & \\ & \rangle 31 \\ 2918 & \\ & \rangle 17 \\ 2901 & \end{array} \qquad\qquad \begin{array}{ll}2974\cdot5 & \\ & \rangle 29\cdot5 \\ 2945\cdot0 & \\ & \rangle 31\cdot5 \\ 2913\cdot5 & \\ & \rangle 16\cdot5 \\ 2897\cdot0 & \end{array}$$

The following are a series of narrow doublets of similar appearance, the constituents of which are equally strong:

$$\left.\begin{matrix}2879\\2877\end{matrix}\right\rangle 2 \qquad \left.\begin{matrix}2875\\2874\end{matrix}\right\rangle 1 \qquad \left.\begin{matrix}2871\\2870\end{matrix}\right\rangle 1 \qquad \left.\begin{matrix}2838\\2836\end{matrix}\right\rangle 2 \qquad \left.\begin{matrix}2834\cdot5\\2832\cdot5\end{matrix}\right\rangle 2$$

The bands 2830, 2828, 2826 are equally strong, and form a group by themselves with a constant difference of about 2 units; and the bands 2815, 2811, 2807 form a group whose most refrangible constituent is the strongest, and there is a constant difference between them of about 4 units.

Photographs of the absorption spectra, in the 2-dcm. tube, of the vapour of the following substances were also taken under varying degrees of temperature and pressure.

Monomethylaniline.

$t°$.	Pressure in mm.	
14°	755	The rays were transmitted to about λ 2500 and then absorbed ; of the Cd lines, 2321, 2313, 2288, 2265, 2194, 2144 were just visible
30	799	The rays were transmitted to about λ 2750 and then absorbed ; the Cd line 2573 was just visible.
45	825	The rays were transmitted to about λ 3050, and then all the rays beyond were absorbed.
60	855	The rays were transmitted to about λ 2990 and then absorbed.
75	885	The rays were absorbed from about λ 3130.
90	915	,, ,, ,, λ 3150.
100	931	,, ,, ,, λ 3165.

Dimethylaniline.

12·5	765	The rays were absorbed from about λ 2500, but the strong Cd lines 2321 to 2144 were just visible.
30	805	The rays were absorbed from about λ 2750, but the Cd line 2573 was visible.
45	835	The rays were absorbed from about λ 3020, although the Cd line 2981 was visible.
60	865	The rays were absorbed from about λ 3070.
75	895	,, ,, ,, λ 3120.
90	925	,, ,, ,, λ 3140.
100	941	,, ,, ,, λ 3170.

Monoethylaniline.

13·5	765	The rays were absorbed from about λ 2470, but the strong Cd lines 2321 to 2144 were just visible.
30	805	The rays were absorbed from about λ 2540.
45	835	,, ,, ,, λ 2700, but the Cd line 2573 was well marked.
60	865	The rays were absorbed from about λ 3050.
75	895	,, ,, ,, λ 3080.
90	925	,, ,, ,, λ 3120.
100	941	,, ,, ,, λ 3150.

Diethylaniline.

12	766	The rays were transmitted to about λ 2450, and the Cd lines 2329 to 2144 were well marked.
100	942	The rays were absorbed from about λ 3150.

o-*Toluidine.*

13	760	The rays were transmitted to about λ 2470 ; the Cd lines from 2329 to 2144 were well marked.
30	804	The rays were transmitted to about λ 2540 ; the Cd lines 2321, 2313, 2288, 2265, 2194, 2144 were visible.
45	830	The rays were transmitted to about λ 2700 ; the Cd line 2573 was just visible.
60	860	The rays were transmitted to about λ 2980 ; the Cd line 2748 was just visible.
75	890	The rays were transmitted to about λ 3060.
90	920	,, ,, ,, ,, λ 3100.
100	936	,, ,, ,, ,, λ 3120.

m-*Toluidine.*

$t°$.	Pressure in mm.	
13	759	The rays were transmitted to about λ 2480 ; the Cd lines 2329 to 2144 were well marked.
45	829	The rays were transmitted to about λ 2750, the Cd line 2748 ending sharply ; the Cd line 2573 was just visible.
75	889	The rays were transmitted to about λ 3050 ; the Cd line 2980 was just visible.
100	935	The rays were transmitted to about λ 3110.

o-3-*Xylidine* (b. p. 223°).

12	752	The rays were transmitted to about λ 2400 ; the Cd lines 2329 to 2144 were well marked.
30	796	The rays were transmitted to about λ 2450 ; the Cd lines 2329 to 2144 were visible.
60	852	The rays were transmitted to about λ 2600 ; the Cd line 2573 was well marked.

m-2-*Xylidine* (b. p. 215°).

12	752	The rays were transmitted to about λ 2250 ; the Cd lines 2194 and 2144 were well marked.
30	796	The rays were transmitted to about λ 2380 ; the series of Cd lines from 2329 to 2144 were well marked.
60	852	The rays were transmitted to about λ 2470 ; the Cd lines from 2329 to 2144 were visible.

Mesidine (b. p. 233°).

13	759	The rays were transmitted to about λ 2350 ; the Cd lines 2321 to 2144 were strong.
45	829	The rays were transmitted to about λ 2420 ; the Cd lines 2321 to 2144 were well marked.
75	889	The rays were transmitted to about λ 2550 ; the Cd lines 2313 and 2268 were just visible.
100	935	The rays were transmitted to about λ 3000 ; the Cd lines 2880, 2837, and 2748 were visible.

Benzylamine.

12·5	752	The rays were transmitted to about λ 2250 ; the Cd lines 2194 and 2144 were well marked.
30	796	The rays were transmitted to about λ 2250 ; the Cd lines 2194 and 2144 were visible.
45	822	The rays were transmitted to about λ 2420 ; the Cd lines from 2329 to 2144 were well marked.
60	852	The rays were transmitted to about λ 2500 ; the Cd lines from 2329 to 2144 were visible.
75	882	The rays were transmitted to about λ 2650 ; the Cd line 2573 was well marked.
90	910	The rays were transmitted to about λ 2900 ; the Cd lines 2880, 2837, and 2748 were visible.

General Results of the Absorption Spectra of the Vapours.

The results of the preceding observations of the absorption spectra of the vapours of aniline and its homologues prove that (1) aniline vapour has a considerable number of absorption bands which show relationships amongst themselves both in structure and in differences of wave-lengths; (2) under the influences of increased temperature and pressure the aniline bands become wider; weak bands become stronger; new bands make their appearance; and the general absorption is shifted towards the less refrangible region; (3) with decreased pressure, the temperature remaining constant, the aniline bands become sharper and weaker, and the region of general absorption is shifted towards the more refrangible region of the spectrum; (4) the most remarkable fact is that none of the homologues of aniline show any of the bands characteristic of aniline; (5) under the influences of increased temperature and pressure, the general absorption of the vapours of the homologues of aniline is shifted towards the less refrangible region.

Solutions.

The experimental methods employed in the study of the absorption spectra of solutions have been described before.

Aniline, Monomethylaniline, and Dimethylaniline.—The ultra-violet absorption spectra of alcoholic solutions of aniline have been described by Hartley and Huntington (*Phil. Trans.*, 1879, **170**, I, 257), who observed two bands at λ 285—λ 274 and λ 240—λ 230. Baly and Collie (Trans., 1905, **87**, 1342) state that they repeated the observations with identically the same results. They also plotted the absorption curves of the bands in alcoholic solutions of mono-methylaniline and dimethylaniline, and they show that the difference in the persistence of the band in the three cases is very marked. The absorption curve of dimethylaniline showed also a second band on the more refrangible side. The author found similar results to those of Baly and Collie in *N*/1000-solutions of these three substances, and the curves are therefore not reproduced.

Monoethylaniline and Diethylaniline.—The author has investigated the absorption spectra of the ultra-violet regions of *N*/1000-alcoholic solutions of these substances. It will be noticed (Fig. 1) that diethylaniline shows a second band at about 1/λ 3850, which is absent in monoethylaniline. It is precisely similar to the phenomena observed by Baly and Collie in mono- and di-methyl-aniline. It is also noticeable that the characteristic band of these substances is not so persistent as the corresponding bands in aniline, mono- and di-methylaniline.

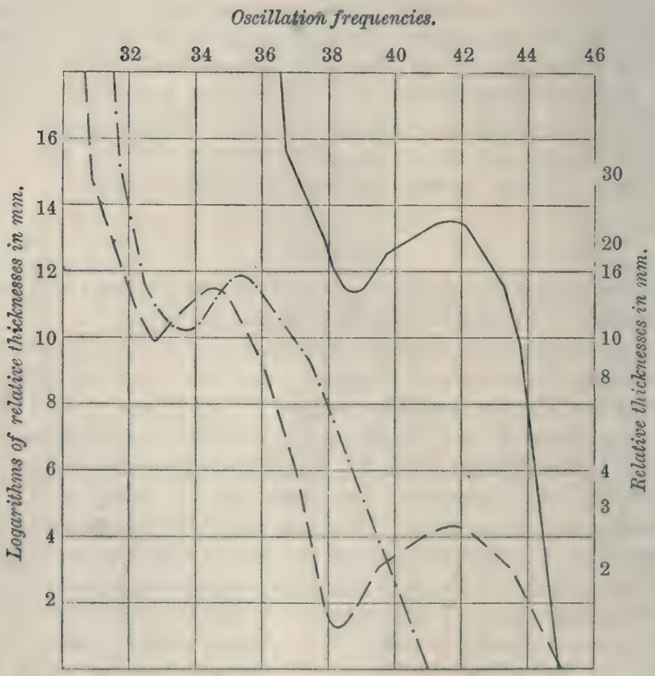
o-*Toluidine.*—Hartley (Trans., 1885, **47**, 685) described a large, persistent band, the head of which was about 1/λ 3040.

m-*Toluidine.*—Baly and Ewbank (Trans., 1905, **87**, 1358) described a large, persistent band, the head of which was about 1/λ 3045.

The author has repeated the observations with *N*/1000-solutions of *o*-toluidine and *m*-toluidine, and found similar results. The curves therefore are not reproduced.

o-3-*Xylidine* and m-2-*Xylidine.*—*N*/1000-alcoholic solutions of these substances were observed, and their absorption curves have been drawn (Fig. 2). The general form of the curves is not unlike that of the toluidines. The bands are strongly persistent, and their positions are more towards the red end than the corresponding bands of the toluidines.

FIG. 1.

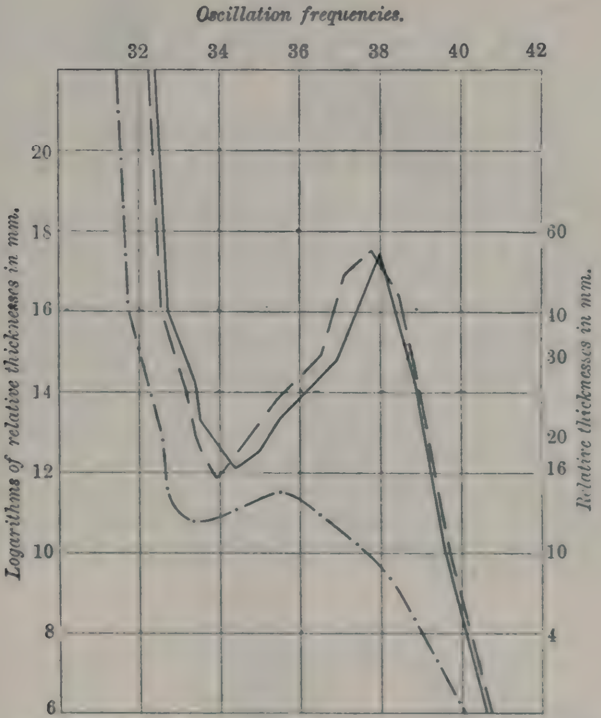


Continuous curve : N/100-*alcoholic solution of benzylamine.*
Dot and dash curve : N/1000-*alcoholic solution of monoethylaniline.*
Dash curve : N/1000-*alcoholic solution of diethylaniline.*

Mesidine.—An *N*/1000-solution of this substance exhibits a band which is not very persistent (Fig. 2). It is of some interest to note that the persistency of this band is not so marked as that of either the toluidines or the xylidines.

Benzylamine.—An *N*/1000-solution transmitted the rays to about λ 2290 through a thickness of 30 mm., but an *N*/100-solution showed a moderately strong band, the curve of which has been drawn (Fig. 1). The position of this band is more towards the regions of greater refrangibility than in any of the substances herein described. It is of some importance to notice that the band corresponds in position and general form with the band 1/λ 3850 of diethylaniline.

FIG. 2.



Continuous curve : N/1000-*alcoholic solution of* o-3-*xylidine.*
Dash curve : N/1000-*alcoholic solution of* m-2-*xylidine.*
Dot and dash curve : N/1000-*alcoholic solution of mesidine.*

General Results of the Absorption Spectra of the Solutions.

The general results of the investigation of the absorption spectra of the solutions are that (1) in the replacement of the hydrogen of the amino-group of aniline by alkyl groups, the persistence of the curve is considerably reduced; (2) when the hydrogen of the nucleus is replaced by alkyl groups the band becomes large and persistent; (3) in mesidine the band is not very strong or persistent; and (4) in benzylamine the band is fairly strong.

Liquids.

Hartley and Huntington (*Phil. Trans.*, 1879, **170**, I, 274) pointed out that it was only on dilution that the absorption bands of aromatic substances became visible. The thickness of the layer of liquid used by them was 0·75 inch.

In investigating the absorbent effect of liquids a special form of cell was used. It consisted of two quartz plates firmly cemented to a brass box or telescope. One of the quartz plates was attached to a movable micrometer screw, which could be moved by thousandths of a mm., whilst the other plate was rigidly attached to a brass stage. A drop of the liquid to be investigated was placed between the two quartz plates, and these were then screwed together to a distance of 0·05 mm. apart. The screw was turned so that the quartz plate attached to it was moved closer and closer to the rigidly placed plate until the distance between them was about 0·001 mm. The light of the Cd spark was passed through the film of liquid for five minutes during each observation. Even through the thinnest films of about 0·001 mm. no absorption bands were seen; and the following numbers state the regions where general absorption began under the above conditions, and through various thicknesses of the films.

Aniline.		*Methylaniline.*		*Dimethylaniline.*		*Ethylaniline.*	
Thickness of film, mm.	λ.	Thickness of film, mm.	λ.	Thickness of film, mm.	λ.	Thickness of film, mm.	λ.
0·050	3185	0·050	3305	0·050	3310	0·050	3260
0·030	3175	0·030	3295	0·030	3300	0·030	3250
0·010	3160	0·010	3270	0·010	3280	0·010	3220
0·004	3150	0·004	3260	0·004	3260	0·004	3210
0·001	3140	0·001	3250	0·001	3270	0·001	3200
Diethylaniline.		o-*Toluidine.*		m-*Toluidine.*		o-3-*Xylidine.*	
0·050	3325	0·050	3150	0·050	3180	0·050	3175
0·030	3310	0·030	3135	0·030	3170	0·030	3165
0·010	3285	0·010	3120	0·010	3140	0·010	3150
0·004	3275	0·004	3100	0·004	3130	0·004	3140
0·001	3265	0·001	3095	0·001	3125	0·001	3130

m-2-Xylidine.		*Mesidine.*		*Benzylamine.*	
Thickness of film, mm.	λ.	Thickness of film, mm.	λ.	Thickness of film, mm.	λ.
0·050	3200	0·050	3250	0·050	2745
0·030	3180	0·030	3210	0·030	2735
0·010	3160	0·010	3160	0·010	2730
0·004	3145	0·004	3140	0·004	2720
0·001	3140	0·001	3130	0·001	2710

General Results of the Absorption Spectra of the Liquids.

The more important points of interest in the above table are that (1) the constitution of the molecules of the various compounds influences the general absorption. For example, the positions of general absorption of the ortho-compounds are different from those of the isomeric meta-compounds; the differences in this respect are comparable with the differences observed in the absorption of their solutions; (2) isomeric substances like benzylamine, the toluidines, and methylaniline show differences in their positions of general absorption, which are also analogous to differences in the absorption of their solutions; (3) none of the substances when in the liquid condition exhibit absorption bands through the thinnest films of 0·001 mm. thick.

It is not possible to imply very much from these numbers, as it is conceivable that films thinner than 0·001 mm. are obtainable under greater pressure, which would allow more of the ultra-violet vibrations to pass through. On the other hand, such excessively thin films produced by pressure could no longer be considered as liquids. The physical condition of the molecules would then be more of the nature of a vapour under high pressure, and the results would hardly be comparable.

Discussion of Results.

In discussing the preceding observations we are confronted with the fact that the vapours of toluene, the xylenes, and mesitylene all exhibit absorption bands as described by Pauer, Grebe (*loc. cit.*), and by Hartley (*Phil. Trans.*, 1908, *A*, **208**, 475), and that the number of bands decreases as the number of methyl groups increases; but in the toluidines, not only do the bands of toluene vapour disappear, but also those characteristic of aniline vapour, and similar phenomena are observed in the xylidines and in mesidine. Further, the replacement of a hydrogen atom of the amino-group in aniline by an alkyl group produces a complete elimination of the bands characteristic of aniline vapour.

In the alcoholic solutions the type of absorption band is very similar in aniline and in the methyl- and ethyl-anilines, whereas in the toluidines and the xylidines the bands are stronger, different in position, and much more persistent than in either toluene, the xylenes, or aniline. The position and intensity of the band in benzylamine is also quite different from that of either toluene or aniline, but it corresponds in form and position with the more refrangible band of diethylaniline.

In the liquids, the general absorption is so great that the ultra-violet light is absorbed over the regions covered by the bands found in the solutions even at thicknesses of the liquids represented by 0·001 mm.

The author has already discussed (*loc. cit.*) the absorption spectra of the vapours of pyridine and some of its derivatives from a consideration of the impacts of symmetrically and unsymmetrically oriented molecules. It seems to be possible to apply a similar explanation to the phenomena described in this communication. In the methyl- and ethyl-anilines the symmetrical orientation of the aniline molecule is distorted, and the vibrations of the more symmetrical aniline, which produce selective absorption, are destroyed. The vibrations producing the absorption bands in the vapours of toluene or the xylenes are wholly different from those producing the bands in aniline vapour; and in the vapours of the toluidines and the xylidines there is no trace of any of the series of bands. The symmetrical orientation of the atoms is absent in these compounds, and the vibrations no longer exercise a selective absorption of the radiant energy. The energy may be chiefly absorbed by the translatory energy of the molecules producing general absorption, which becomes more pronounced as the temperature and pressure are increased.

In the solutions, the solvent acts partly as a constraint on the vibrations of the molecules of the dissolved substance, partly as a barrier to the number of encounters, and partly as an absorbent of a portion of the radiant energy. The result of these influences is that the vibrations of the molecules are quite different from those of the vapours. The atoms of the molecules under these conditions vibrate or oscillate in a definite way characteristic of each substance; and molecules of the same type, for example, aniline and the methyl- and ethyl-anilines, exhibit bands having similar forms. They differ only in their relative positions and in their increased or decreased persistencies, which are regulated by the number, weight, and type of the substituted groups.

In the liquids, the molecules are more closely packed, and they exert a greater tensional effect on each other, so that the restraining influences on the vibrations are still more powerful. The radiant energy is absorbed by the molecules, for even when the film of liquid was only 0·001 mm. thick, no bands of selective absorption were observed in any of the liquids. Nevertheless, the differences observed in the positions of general absorption of the ortho- and meta-compounds and in the isomeric substances, benzylamine, methylaniline, and the toluidines, indicate that, besides the weight of the molecule, the orientation is also a factor in determining the extent of the general absorption as distinct from selective absorption.

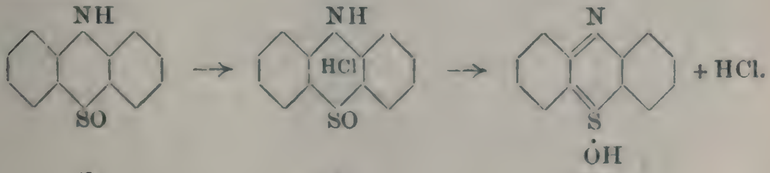
I have again to convey my thanks to the Government Grant Committee of the Royal Society, by whose assistance the larger portion of the cost of the apparatus used in these experiments was defrayed.

University Chemical Laboratory,
Cambridge.

CXLIV.—*The Intramolecular Rearrangement of Diphenylamine* ortho-*Sulphoxides. Part III. The Tri- and Tetra-chlorosulphoxides.*

By Oscar Lisle Brady and Samuel Smiles.

In the previous communication on this subject (Barnett and Smiles, this vol., p. 186) the mechanism of this reaction was discussed, and it was shown that the rearrangement, which is brought about by the action of acids on the sulphoxides of diphenylamine, probably depends on the preliminary formation of salts of these substances (II):



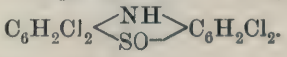
(I.) (II.) (III.)

In order to obtain complete confirmation of this hypothesis, it is evidently desirable to isolate these sulphoxide salts and to examine their independent behaviour; but in none of the six cases which have been studied has this been possible. In those instances where the sulphoxide was sufficiently basic to give promise that the salts would be readily formed, the conversion into the phenazothionium derivative was too rapid to permit of their being isolated, and in other cases, where this conversion is slow, the sulphoxides were of acidic character or such extremely weak bases that no hope of isolating the salts in the pure condition could be entertained.

It has been shown that the conversion of the sulphoxide into the phenazothionium derivative depends on the nature of the groups present in the aromatic nuclei (Barnett and Smiles, this vol., p. 192) of the former, and it appeared not improbable that, in accordance with the usual phenomena of steric hindrance, the mere presence of substituents, whatever their nature, would exert a retarding influence on this change. With this assumption, it is clear that in order to isolate the required salts a sulphoxide must be chosen containing substituents which do not to any great extent depress the basic character of the parent substance, and are present in sufficient number to prevent the conversion into the phenazothionium derivative taking place too readily. Since the chloro-derivatives of thiodiphenylamine appeared to satisfy these requirements, the following experiments were undertaken with them.

Tetrachlorothiodiphenylamine is easily prepared in large quantities by the simultaneous action of hydrochloric acid and hydrogen dioxide on thiodiphenylamine (Page and Smiles, this vol., p. 1112). This substance was converted into the sulphoxide in the usual manner by the further action of hydrogen dioxide.

Tetrachlorodiphenylamine o-*Sulphoxide*,



$$C_6H_2Cl_2{<}{\substack{NH\\SO}}{>}C_6H_2Cl_2.$$

Tetrachlorothiodiphenylamine was suspended in glacial acetic acid, to which an excess of 30 per cent. hydrogen dioxide had been added. The mixture was set aside at the atmospheric temperature for three or four days. The completion of the reaction was indicated by the disappearance of the characteristic crystals of the sulphide, which were replaced by a very finely divided precipitate. This was collected, and, after the adherent acetic acid had been removed, the solid was recrystallised from benzene. In this way tetrachlorodiphenylamine-*o*-sulphoxide was obtained in colourless prisms, which melted at 220°, the fused mass assuming a reddish-brown colour:

0·1304 gave 0·1931 CO_2 and 0·0186 H_2O. $C = 40·4$; $H = 1·6$.

$C_{12}H_5ONCl_4S$ requires $C = 40·8$; $H = 1·4$ per cent.

The presence of the sulphoxide grouping in this compound is proved by the condensation with phenetole to the *S*-phenetyl derivative, which is described later.

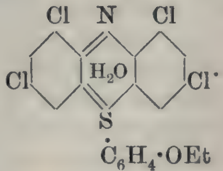
This sulphoxide has been previously prepared, although evidently in an impure condition, by Unger and Hofmann (*Ber.*, 1896, **29**, 1362) from the action of nitric acid on tetrachlorothiodiphenylamine. These authors find that, as usual, the bivalent sulphur is oxidised to the sulphoxide group by that reagent, but that, unless special precautions are taken, a portion of the halogen is displaced by nitro-groups. We have repeated these experiments, and, whilst confirming the observations of Unger and Hofmann, find that the method is not suitable for preparing the pure sulphoxide in large quantity. The product is usually red, and is evidently contaminated with the phenazothionium derivative, which, as will be shown later, is obtained from the sulphoxide by the action of strong acids.

The conversion of this tetrachlorosulphoxide into the phenazothionium hydrate appears to be effected with approximately the same ease as that of the dinitro-sulphoxide (Barnett and Smiles, Trans., 1909, **95**, 1261). It is not attacked by dilute mineral acids, and only slowly by hot concentrated hydrochloric acid. In sulphuric acid the reaction is slow, and it can be followed by the change in colour and by the reactions of the solutions. Freshly prepared solutions of the sulphoxide in the concentrated acid, which are of a deep yellowish-brown colour, evidently still contain the sulphoxide, for, on adding phenetole or a similar substance to them, the *S*-arylphenazothionium derivative is formed. However, after the lapse of about four hours, these solutions become violet, and the *S*-phenetyl derivative cannot then be obtained by the addition of phenetole; on pouring the solution into water, the tetrachlorophenazothionium hydrate is precipitated.

*Tetrachloro-*S*-phenetylphenazothionium.*

An excess of phenetole was gradually added to a cold solution of tetrachlorodiphenylamine sulphoxide in concentrated sulphuric acid. The course of the reaction is indicated by the appearance of an intense blue colour, and, as soon as it was found that a sample of the solution gave a precipitate of a pure reddish-brown colour on being mixed with water, the addition of phenetole was suspended. On pouring the solution into water, the required derivative was precipitated; it was collected, washed with water, and then converted into the base by trituration with dilute aqueous sodium hydroxide. The substance was again collected, and, after being washed with water until free from alkali, it was dried in the steam-oven, and finally extracted with chloroform in Soxhlet's apparatus. The cold extract deposited tetrachloro-*S*-phenetylphenazothionium hydrate (IV) in chocolate-coloured prisms, which melted at 197°.

The substance, when prepared in this manner, evidently contains chloroform of crystallisation, for a sample which had been dried for



(IV.)

some hours in the steam-oven readily furnished phenylcarbylamine when warmed with aniline and alkali hydroxide. Analysis confirmed this suspicion:

0·1326 gave 0·2047 CO_2 and 0·0242 H_2O. C = 42·2; H = 2·3.
0·1197 „ 0·1851 CO_2 „ 0·0217 H_2O. C = 42·2; H = 2·0.
$C_{20}H_{13}ONSCl_4,H_2O$ requires C = 50·5; H = 3·1 per cent.
$C_{20}H_{13}ONSCl_4,H_2O,CHCl_3$ requires C = 42·4; H = 2·8 per cent.

This additional chloroform is very firmly retained by the substance, for on heating a sample for several hours at 140—150°, only slight loss of weight occurred, and analysis showed that almost the theoretical amount of halogen was still present:

0·1074 gave 0·1697 AgCl. Cl = 39·1.
$C_{20}H_{13}ONSCl_4,H_2O,CHCl_3$ requires Cl = 41·8 per cent.

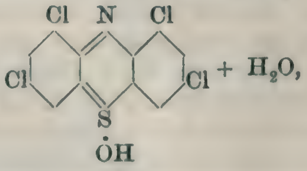
The substance is insoluble in water, sparingly soluble in ether, and readily so in other warm organic media. It imparts an intense blue colour to sulphuric acid.

Tetrachlorophenazothionium.

A solution of tetrachlorodiphenylamine *o*-sulphoxide in concentrated sulphuric acid was kept at the atmospheric temperature for four or five hours, when it was poured on ice, and the mixture set aside overnight to obtain complete separation of the insoluble material. The latter was then collected, and, after being purified and dried at 100°, it was analysed:

0·1066 gave 0·1532 CO_2 and 0·0181 H_2O. C = 39·1; H = 1·9.
$C_{12}H_5ONSCl_4,H_2O$ requires C = 38·8; H = 1·8 per cent.

Tetrachlorophenazothionium hydroxide (V),



(V.)

which is obtained in this way as a brownish-red powder, resembles other hydroxides of this series in containing an additional molecule of water (this vol., p. 186). The latter is not readily eliminated; in fact, it is only on heating to about 180° that water is expelled, the compound melting somewhat indefinitely at 200°. The substance is insoluble in water, but soluble in hot glacial acetic acid. The solutions in sulphuric acid are purple, and do not react with phenetole or similar compounds. This azothionium derivative may also be prepared by direct oxidation of the tetrachloro-sulphide in acid media.

Oxidation of Tetrachlorothiodiphenylamine.—(*a*) *With Chromic Acid.*—A hot solution of tetrachlorothiodiphenylamine was gradually mixed with the calculated amount of chromic acid dissolved in the same medium. The mixture was set aside to cool, and then poured into cold water, the insoluble product being collected and recrystallised from benzene. This was analysed (1).

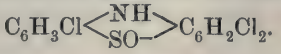
(*b*) *With Caro's Reagent.*—The calculated amount of potassium persulphate was slowly added to a cold mixture of tetrachlorothiodiphenylamine and concentrated sulphuric acid. The liquid was poured over crushed ice, and then set aside until the product was completely precipitated. The latter was collected, washed with water until free from sulphuric acid, then dried, and finally recrystallised from hot ethyl acetate. The substance was analysed (2). The product obtained by these two methods forms dark red prisms, which melt at 220°, and give purple solutions with concentrated sulphuric acid:

(1) 0·2142 gave 0·3316 CO_2 and 0·0294 H_2O. C = 42·2; H = 1·5.
    0·1046 „ 0·1700 AgCl. Cl = 39·4.
(2) 0·1406 „ 0·2184 CO_2 and 0·0216 H_2O. C = 42·3; H = 1·7.

It is evident from the analytical data that the substance is not the phenazothionium hydroxide (C = 38·8 and H = 1·8 per cent.) which is obtained by rearrangement of the sulphoxide. According to the numbers which are quoted above, the compound would appear to be either an oxide derived from the phenazothionium hydroxide by separation of the elements of water (C = 41·8 and Cl = 41·2 per cent.) or a compound of the nature of a quinhydrone composed of equal molecular proportions of sulphide and azothionium hydroxide (C = 41·7 and Cl = 41·1 per cent.). The latter alternative appears to be the more probable, but since this question lies outside the scope of the present experiments it has not been further pursued.

The tetrachloro-sulphoxide, the derivatives of which have now been described, is not a sufficiently strong base to furnish stable salts with acids, and attention was therefore turned to the trichloro-derivative.

Trichlorodiphenylamine o-Sulphoxide,



$$C_6H_3Cl<\begin{matrix}NH\\SO-\end{matrix}>C_6H_2Cl_2.$$

In the chlorination of thiodiphenylamine by the action of hydrogen dioxide and hydrochloric acid in alcoholic solution (Page and Smiles, this vol., p. 1118), it was sometimes observed that the yield of tetrachloro-sulphide was considerably below that required by theory. Since this substance is almost insoluble in the alcoholic mother liquor obtained in this preparation, it appeared probable that the loss might be due to incomplete chlorination, hence the more soluble substances produced in this reaction were examined. These were isolated by pouring the filtered mother liquor into a large bulk of water; the solid was collected, washed, dried, and finally recrystallised from hot benzene. The trichloro-sulphoxide was isolated from the less soluble portion obtained in this process. It is readily soluble in hot benzene, and was obtained in prismatic crystals, which melted at 160°. It is soluble in concentrated sulphuric acid, immediately producing an intense violet colour, and when the solution is mixed with water the reddish-brown azothionium derivative is obtained:

0·1125 gave 0·1870 CO_2 and 0·0218 H_2O. $C=45·3$; $H=2·1$.

$C_{12}H_6ONCl_3S$ requires $C=45·2$; $H=1·9$ per cent.

The *hydrochloride* of this sulphoxide was also isolated from the mother liquors of the preparation of tetrachlorothiodiphenylamine by cautiously adding water to them and setting the mixture aside until the precipitate had formed. The substance was purified and dried for analysis in a vacuous desiccator:

0·1210 gave 0·1785 CO_2 and 0·0133 H_2O. $C=40·2$; $H=1·2$.

0·1167 „ 0·1897 AgCl. $Cl=40·2$.

$C_{12}H_6ONCl_3S,HCl$ requires $C=40·5$; $H=1·9$; $Cl=40·0$ per cent.

It forms a pale grey powder, which is soluble in concentrated sulphuric acid, giving purple solutions, and evolving hydrogen chloride; the latter is also eliminated when the compound is boiled with water.

The corresponding *trichlorophenazothionium* derivative is formed when this hydrochloride is heated either alone to about 100° with water, or in boiling media, such as benzene or ethyl acetate. Prolonged heating decomposes the product, which is therefore difficult to isolate in a pure state. A weighed quantity of the hydrochloride was suspended in cold water, and the mixture was heated to the boiling point. The reddish-brown product was immediately collected and washed with cold water, the filtrates being collected. Analysis of the product, which melted indefinitely at 125—130°, and gave the usual reaction of phenazothionium derivatives with sulphuric acid, showed that it was the partly hydrolysed phenazothionium chloride, and this was confirmed by estimation of the free hydrochloric acid in the mother liquors:

0·1136 gave 0·1740 CO_2 and 0·0197 H_2O. C = 41·8; H = 2·0.

$C_{12}H_5NCl_4S,H_2O$ requires C = 42·8; H = 2·3 per cent.

Further attempts to purify this compound by more prolonged boiling with water or by treatment with alkali hydroxide were not successful on account of its instability towards these reagents.

The fact that this hydrochloride is so readily converted into the azothionium derivative adds further support to the hypothesis already advanced on other grounds that in the change of these sulphoxides of diphenylamine to the azothionium compounds by the action of acids the salts of the former are first produced.

In conclusion, we desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed the expenses of these experiments.

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CXLV.—*The Action of Bases on αβ-Dibromobutyric Acid and its Esters.*

By Thomas Campbell James.

In a previous communication (James and Sudborough, Trans., 1909, **95**, 1543) it was established that when hydrogen bromide is abstracted from αβ-dibromo-β-phenylpropionic acid (cinnamic acid dibromide) by the action of feeble bases and alkaloids, the yield of α-bromocinnamic acid is comparatively much greater, and the amount of α-bromo*allo*cinnamic acid correspondingly diminished, than when strong alkalis are used. Thus, when the decomposition is effected by alcoholic potassium hydroxide in the cold, the ratio α-bromocinnamic acid/α-bromo*allo*cinnamic acid is, roughly, 1/7, whereas with trimethylamine it is about 1/2. An increase in the relative amount of the α-bromo-acid also occurs in experiments with weak bases where heat is required to complete the reaction, but in these cases a considerable amount of decomposition takes place with formation of α-bromostyrene and evolution of carbon dioxide, and the precise degree of transformation of *allo*-acid into its stereoisomeride is thereby obscured. It has been shown by following the reaction between aqueous alkali and αβ-dibromobutyric acid, kinetically, that the tendency towards decomposition is less in this case than in the above, and a series of experiments has therefore been carried out to investigate the action of various bases on this acid.

αβ-Dibromobutyric acid, $CH_3{\cdot}CHBr{\cdot}CHBr{\cdot}CO_2H$, was obtained by Körner (*Annalen*, 1866, **137**, 234) by the addition of bromine to crotonic acid. Its preparation is described in detail by Michael and Norton (*Amer. Chem. J.*, 1881, **2**, 11) and by Kolbe (*J. pr. Chem.*, 1882, [ii], **25**, 386). By abstracting hydrogen bromide by means of alkali, Michael and Norton obtained a bromocrotonic acid, melting at 92°, isomeric with the acid, melting at 106·5°, obtained by the same observers from αα-dibromobutyric acid. Erlenmeyer and Müller (*Ber.*, 1882, **15**, 49) showed that when αβ-dibromobutyric acid was decomposed with two equivalents of alcoholic potassium hydroxide, a mixture of the two bromocrotonic acids is obtained. These were separated by taking advantage of the great difference in the solubility of their potassium salts in absolute alcohol, when about 10 per cent. of the acid melting at 106·5° was obtained. Wislicenus (*Annalen*, 1888, **248**, 322), who described both acids as α-bromocrotonic acids, used aqueous potassium hydroxide for the decomposition, and obtained a large proportion of α-bromo*allo*crotonic acid, melting at 92°, with a slight amount of α-bromocrotonic acid, melting at 106·5°.

Michael and Schulthess (*J. pr. Chem.*, 1892, [ii], **46**, 257) confirm the results obtained by Wislicenus, and give quantitative data. Two experiments are described, wherein 10 grams of αβ-dibromobutyric acid were decomposed with two equivalents of aqueous potassium hydroxide, one carried out at low temperature (0—10°) and the other at 35°. Separating the products by crystallising their potassium salts from ten times their weight of absolute alcohol, they obtained 3·5 per cent. of α-bromo-salt and 96·5 per cent. of α-bromo*allo*-salt in each case.

It has been shown by Sudborough and Thompson (Trans., 1903, **83**, 671) and by Michael (*Ber.*, 1901, **34**, 3666) that the replacement of the acidic hydrogen of αβ-dibromo-β-phenylpropionic acid by alkyl groups has a profound effect on the decomposition by means of alkalis, the yield of α-bromocinnamic acid being greatly increased in the case of all the esters used. Michael and Browne (*Amer. Chem. J.*, 1887, **9**, 280) state that a similar effect is noticed when the ethyl ester of αβ-dibromobutyric acid is similarly decomposed, but the results given in this paper indicate that the effect is not so marked as stated by them.

The experimental work described in this paper may be classified under the following heads:

I. Determination of the rate of decomposition of certain αβ-dibromo-acids by aqueous potassium hydroxide.

II. The action of bases on αβ-dibromobutyric acid under varying conditions.

III. The preparation of esters of αβ-dibromobutyric acid.

IV. Decomposition of the esters by potassium hydroxide.

I.—*The Rate of Decomposition of certain αβ-Dibromo-acids by Aqueous Potassium Hydroxide.*

The constants of the reactions

$$X{\cdot}CHBr{\cdot}CHBr{\cdot}CO_2K + KOH \longrightarrow X{\cdot}CH{:}CBr{\cdot}CO_2K + KBr + H_2O$$

($X = H$, CH_3, or C_6H_5) have been determined in aqueous solution at 15°. The general method was to treat a weighed quantity of the finely powdered acid very gradually with one equivalent of pure aqueous potassium hydroxide solution. This was made up to a known volume, and, after being kept for some time in a thermostat at 15°, a second equivalent of alkali was added. Known volumes of the mixture were titrated at definite intervals with standard sulphuric acid.

i. *Dibromopropionic Acid*, $CH_2Br{\cdot}CHBr{\cdot}CO_2H$.—This acid was prepared from allyl alcohol, as described by Tollens and Münder, etc. (*Annalen*, 1873, **167**, 224, 241). After crystallising from light petroleum, it melts at 63—64°.

Series A.—Initial concentration of reacting substances, $N/40$; 80 c.c. were titrated at intervals with $0{\cdot}0969N$-sulphuric acid. $a = 20{\cdot}65$ c.c.

Time in hours.	$a-x$.	x.	$k = 1/t \dfrac{x}{a(a-x)}$.
0·417	8·55	12·10	0·1645
0·583	7·10	13·55	0·1602
0·917	5·00	15·65	0·1653
2·00	2·70	17·95	0·1610
		Mean.........	0·1627

$$\text{For } N\text{-solution, } k = 0{\cdot}1627 \times \frac{80}{0{\cdot}0969} = 134{\cdot}4$$

Series B.—Initial concentration of the reacting substances, $N/50$; 20 c.c. were titrated at intervals with $0{\cdot}01211N$-sulphuric acid. $a = 29{\cdot}50$ c.c.

Time in hours.	$a-x$.	x.	k.
0·333	16·50	13·00	0·08080
0·833	9·80	19·70	0·08180
		Mean.........	0·08130

$$\text{For } N\text{-solution, } k = 0{\cdot}0813 \times \frac{20}{0{\cdot}01211} = 134{\cdot}2$$

Mean of Series A and $B = 134{\cdot}3$

ii. *αβ-Dibromobutyric Acid.*—This acid was prepared as described by Michael (*loc. cit.*), and, after crystallising from carbon disulphide, melted at 87°.

Series A.—Initial concentration of the reacting substances, $N/8$ approx.; 20 c.c. were titrated at intervals with 0·0969N-sulphuric acid. $a = 24·32$ c.c.

Time in hours.	$a-x$.	x.	$k = 1/t \frac{x}{a(a-x)}$.
1·00	17·00	7·32	0·1770
1·53	14·60	9·72	0·1789
2·00	12·95	11·37	0·1805
3·33	9·80	14·52	0·1830
6·00	6·80	17·52	0·1765
7·50	5·75	18·57	0·1770
		Mean	0·1788

$$\text{For } N\text{-solution, } k = 0·1788 \times \frac{20}{0·0969} = 3·69$$

Series B.—Initial concentration of reacting substances, $N/10$ approx.; 20 c.c. were titrated at intervals with 0·0969N-acid. $a = 19·60$ c.c.

Time in hours.	$a-x$.	x.	k.
0·5	16·80	2·80	0·01700
2·0	11·79	7·81	0·01690
3·0	9·86	9·74	0·01680
4·0	8·25	11·35	0·01754
		Mean.........	0·01706

$$\text{For } N\text{-solution, } k = 0·01706 \times \frac{20}{0·0969} = 3·52$$

Mean of Series A and $B = 3·60$

iii. *αβ-Dibromo-β-phenylpropionic Acid*, $C_6H_5·CHBr·CHBr·CO_2H$.—Initial concentration of the reacting substances, $N/25$ approx.; 50 c.c. of the solution were titrated at intervals with 0·0969N-acid. $a = 19·10$ c.c.

	Time in hours.	$a-x$.	x.	$k = 1/t \frac{x}{a(a-x)}$.
(1)	1·083	18·10	1·00	0·00267
(2)	2·50	17·00	2·10	0·00259
(3)	5·00	15·10	4·00	0·00277
(4)	19·00	8·25	10·85	0·00362
(5)	23·00	6·86	12·24	0·00406
		Mean of (1), (2), and (3)............		0·00268

$$\text{For } N\text{-solution, } K = 0·00268 \times \frac{50}{0·0969} = 1·38$$

In the later stages (4) and (5) the odour of α-bromostyrene was distinctly observable, indicating partial decomposition, thus accounting for the high values of k.

From these experiments it is seen that the rate of elimination of hydrogen bromide from αβ-dibromo-acids is considerably affected by the presence of alkyl groups in the β-position, and depends also on the nature of these groups. The ratios of the constants in the above experiments are:

$$H : Me : Ph : : 100 : 2{\cdot}68 : 1{\cdot}03.$$

It is also apparent that the decomposition of $\alpha\beta$-dibromopropionic and $\alpha\beta$-dibromobutyric acids by means of potassium hydroxide in dilute aqueous solution at 15° is not complicated by side-reactions.

II.—*The Action of Bases on αβ-Dibromobutyric Acid under Varying Conditions.*

A series of experiments has been performed with the view of ascertaining the variation in the proportion of the two α-bromocrotonic acids obtained by abstracting hydrogen bromide from $\alpha\beta$-dibromobutyric acid with different bases under varying conditions. The acid is obtained in theoretical yield by the method described by Michael and by Kolbe, which consists in adding a slight excess of bromine to crotonic acid dissolved in carbon disulphide, keeping for several hours, and then evaporating off the solvent. On crystallising from carbon disulphide or light petroleum, the pure acid, melting at 87°, is obtained.

As mentioned above, quantitative results for the action of alcoholic and aqueous potassium hydroxide have been given by Erlenmeyer and Müller and by Michael and Schulthess. Working in alcoholic solution, the former obtained 10 per cent. of α-bromocrotonic acid, whilst, in aqueous solution, the latter only obtained 3·5 per cent. of this product. Both results are confirmed in the present paper.

The method of separation of the isomerides, as described by Michael and Schulthess, has been tested as follows: 2 grams of α-bromocrotonic acid and a similar weight of α-bromo*allo*crotonic acid were mixed and dissolved in 40 grams of absolute alcohol (99·8 per cent.). The solution was titrated with a 10 per cent. solution of alcoholic potassium hydroxide until neutral, and kept in a dark cupboard for two hours, by which time a copious separation of potassium α-bromocrotonate had occurred The precipitate was collected on to a weighed filter, washed five times with small quantities of alcohol, and dried in a steam-oven to constant weight, which was 2·48 grams (theory, 2·46 grams). The filtrate was evaporated to dryness, and the residue of potassium α-bromo*allo*crotonate weighed 2·45 grams. The separation is therefore complete within 1 per cent.

In studying the action of bases on $\alpha\beta$-dibromobutyric acid, the general method has been to act on 10 grams of the acid with two molecular proportions of the base until the reaction is completed.

When alcoholic solutions were used, the reaction mixture was then evaporated on a water-bath to remove alcohol, acidified with dilute hydrochloric acid, and extracted five times with ether. After drying, the ethereal solution was evaporated in a vacuum desiccator to constant weight, and the yield of α-bromo-acids noted. The latter were then dissolved in ten times their weight of absolute alcohol, and titrated with a 10 per cent. solution of alcoholic potassium hydroxide until neutral. After being kept for two to three hours in the dark, the very sparingly soluble potassium α-bromocrotonate was collected on a weighed filter, washed several times with small quantities of absolute alcohol, dried in a steam oven, and weighed. The filtrate was evaporated on a steam-bath, dried to constant weight in the steam-oven, and the weight of potassium α-bromo*allo*crotonate determined. In a few cases the latter was determined by difference.

The results for the alkalis used, expressed as percentage yields of the acids obtained, are given in the following table:

Ten grams of αβ-dibromobutyric acid treated with two equivalents of alkali (strength approx. normal except where otherwise stated).

Alkali.	Conditions.	Per cent. yield of α-bromo-crotonic acid.	Per cent. yield of α-bromo-*allo*crotonic acid.	Total yield.
Potassium hydroxide, aqueous	10—15° for 24 hours	3·35	92·15	96·50
,, ,, ,,	15 min. on gently boiling water-bath	6·54	86·60	93·15
,, ,, alcoholic	10—15° for 24 hours	9·45	86·55	96·00
Sodium hydroxide, aqueous...	10—15° for 3 days...	8·50	87·50	96·00
,, ,, ,, ...	,, ,, ...	10·40	86·60	97·00
,, ,, ,, ...	20 min. on gently boiling water-bath	6·55	87·45	95·00
,, ,, ,, ...	20 min. on gently boiling water-bath	7·03	85·77	92·80
Ammonia, aqueous 3*N*	10—15° for 12 days	Decomposition incomplete		
,, ,, ...	,, ,, 6 weeks	24·60	59·90	84·50
,, ,, ...	50—60° for 6 hours	4·80	50·70	55·50
,, ,, ...	40—50° ,, 6 ,,	7·00	58·00	65·00
Ammonia in methyl-alcoholic solution, 3*N*.	4 months at ordinary temperature	Decomposition incomplete		
	15 min. on boiling water-bath	8·10	51·90	60·00

The α-bromo- and α-bromo*allo*-crotonic acids were recovered from the potassium salts in each case, and, after recrystallising once from water, melted at 106—107° and 92° respectively.

Experiments were also carried out with the following tertiary bases and alkaloids.

Trimethylamine.—Eight grams of αβ-dibromobutyric acid were treated with 4·0 grams of trimethylamine (two equivalents) in 25 c.c. of methyl alcohol, a rise of temperature taking place on mixing. After a week the mixture was worked up as described above, and yielded an 84 per cent. yield of α-bromocrotonic acids, consisting of 45 per cent. of α-bromo- and 39 per cent. of α-bromo-*allo*-acid.

The remaining experiments were carried out with absolute ethyl alcohol as solvent. Ten grams of αβ-dibromobutyric acid were treated with a solution of two equivalents of the base in 50 or 100 c.c. of alcohol, and warmed in a reflux apparatus over a gently boiling water-bath for a definite time. The alcohol was then evaporated off, and the products worked up as usual. The results are given in the following table:

Base.	Volume of solvent, in c.c.	Time of heating, in hours.	Per cent. of α-bromo-acid.	Per cent. of α-bromo-*allo*-acid.	Per cent. of total yield.
Dimethylaniline ...	100	1	21·2	45 5 *	70·0
,, ...	50	1	22 5	74·5	97·0
Pyridine	50	1¼	16·7	65·2	81·9
,, ...	50	1	20 5	71·0	91·5
Quinoline	50	1	12·7	63 3	76·0
Brucine...............	100	1½	18·9	29·3 *	50 7
,, ...	100	1	25·5	34·0 *	60·5
,, ...	100	¾	34·5	32·0	66·5
,, ...	100	¼	Decomposition incomplete		
Cinchonidine	100	1	—	—	64·8
,, ...	100	⅔	9·7	60·7	70·4
Quinine...............	100	¾	10·9	53·2	64·1

* Slight loss in these cases.

Control experiments carried out with dimethylaniline showed that neither α-bromocrotonic acid nor α-bromo*allo*crotonic acid is transformed into its isomeride under the conditions of the experiment. Two grams of each acid were separately warmed with two equivalents of the base in alcohol solution for an hour. After working up in the usual manner, 1·80 grams and 1·75 grams respectively of the two acids were recovered, and no trace of the isomerides.

It was noticed, however, that when alcoholic solutions of potassium α-bromo*allo*crotonate were kept for extended periods of time, a gradual transformation into the sparingly soluble α-bromocrotonate occurred. Thus, a solution of 2 grams of the *allo*-salt dissolved in 20 grams of absolute alcohol deposited 0·27 gram of the isomeride during the course of three weeks.

No definite conclusions can be drawn from the results obtained, but, considered generally, the yield of α-bromocrotonic acid is greater the weaker the base used for abstracting hydrogen bromide.

III.—*Preparation of Esters of αβ-Dibromobutyric Acid.*

Ethyl Ester.—Michael and Browne (*loc. cit.*) describe the preparation of the ethyl ester, which was obtained by saturating a solution of one part of the acid in three parts of absolute alcohol with dry hydrogen chloride, the solution being cooled to 0°. After twenty-four hours, the liquid was poured into water and extracted with ether, the ethereal solution shaken with sodium carbonate solution, and dried over calcium chloride. By distillation under diminished pressure, they obtained a heavy oil, boiling at 113—114°/30 mm.

This preparation has been repeated three times, using 20 grams of acid for each experiment, and keeping the mixture for three days. In each case a 60 per cent. yield of ester, consisting of a heavy, colourless liquid, boiling at 123—124°/30 mm., was obtained. (Found, Br = 58·35. Calc., Br = 58·40 per cent.)

Methyl Ester.—This ester was obtained by a method similar to the above; it is a colourless liquid, boiling at 103°/15 mm. and 125°/48 mm. It was analysed by Stepanow's method:

0·2926 required $22\cdot56N/10\text{-AgNO}_3$. Br = 61·59.

$C_5H_8O_2Br_2$ requires Br = 61·49 per cent.

Allyl Ester.—This was prepared by dissolving 20 grams of the acid in 50 grams of allyl alcohol, and saturating the solution with dry hydrogen chloride at 0°. After three weeks the lower layer of ester was separated, dissolved in ether, washed with dilute sodium carbonate solution and with water, and dried. The ether was removed, and the ester distilled under diminished pressure. A 65 per cent. yield of a colourless, heavy liquid, boiling at 141·5°/30 mm., was obtained:

0·3795 gave 0·4958 AgBr. Br = 55·62.

$C_7H_{10}O_2Br_2$ requires Br = 55·94 per cent.

IV.—*Decomposition of the Esters with Potassium Hydroxide.*

Michael and Browne (*loc. cit.*) state that when ethyl $\alpha\beta$-dibromobutyrate is decomposed with two equivalents of alcoholic potash by warming for a few minutes on a water-bath, the chief product is α-bromocrotonic acid, the remainder being a small amount of an acid which was not identified. A series of experiments carried out with the esters described above shows that the increase in the relative amount of α-bromo-acid obtained in this case is not nearly as great as supposed by Michael, and differs greatly in this respect from the analogous decomposition of cinnamic acid dibromide (compare Sudborough and Thompson, *loc. cit.*).

Ethyl Ester.—Ten grams of the ester were dissolved in an equal weight of absolute alcohol, and treated with two equivalents of 10 per cent. alcoholic potassium hydroxide. After being kept overnight at 10—15°, the alcohol was evaporated off, the acids precipitated with dilute hydrochloric acid, extracted with ether, and separated as previously described. Three experiments were performed:

	α-Bromo-acid, per cent.	α-Bromo*allo*-acid, per cent.	Total yield, per cent.
(1)	17·6	74·6	92·2
(2)	20·7	79·3	100·0
(3)	20·3	76·7	97·0

Methyl Ester.—Three experiments were carried out under similar conditions to the above, using methyl-alcoholic potassium hydroxide. The total yields of product were respectively 95·8, 100, and 100 per cent., the crude acid melting in each case at 89—90°. When separation was attempted in the usual manner, no trace of potassium α-bromocrotonate separated out after keeping for three hours. The product therefore consists entirely of *allo*-acid.

Allyl Ester.—One experiment was performed, in which 10 grams of the ester were dissolved in acetone, and then treated with two equivalents of aqueous potassium hydroxide, sufficient acetone being added to render the solution homogeneous. After keeping overnight, the acetone was evaporated off, and the solution acidified, the acids being extracted and separated as usual. A total yield of 88·9 per cent. of the mixed acids was obtained, consisting of 14·4 per cent. of α-bromocrotonic acid and 74·5 per cent. of α-bromo*allo*crotonic acid.

The author is indebted to Dr. J. J. Sudborough for his advice and interest in this research.

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CXLVI.—*Freezing-point Curve for Mixtures of Camphor and Phenol.*

By JOHN KERFOOT WOOD and JANET DRUMMOND SCOTT.

PHARMACOLOGISTS are well acquainted with the fact that when a small amount of camphor is added to phenol, the mixture assumes the liquid state, and remains in that condition even when cooled to temperatures considerably below the freezing point of phenol. This liquefaction might simply be due to the camphor dissolving in the phenol, thereby lowering the freezing point of the latter; a second reason for the liquefaction might be the formation of a compound of the two substances, the freezing point of the compound being lower than that of phenol. Léger (*Compt. rend.*, 1890, **111**, 109) has stated that phenol and camphor unite to form two compounds, a monocamphoride melting at −23°, and a hemicamphoride which remained in the liquid state even when cooled to −50°. Should these statements be correct, the liquefaction which succeeds the addition of camphor to phenol is easily explained. A reference to Léger's paper will show, however, that these conclusions were drawn from what, according to modern physico-chemical ideas, would be regarded as very slight and insufficient experimental evidence. This fact, coupled with the natural interest of the subject, and the additional fact that statements of Léger's relating to mixtures of camphor with the naphthols and other phenolic substances have recently been disproved by Caille (*Compt. rend.*, 1909, **148**, 1458), led the authors to re-investigate the subject.

In any such investigation, trustworthy results can only be obtained by examining the behaviour of a large number of mixtures containing the two components in varying proportions. By constructing, therefore, the complete freezing-point curve for all mixtures ranging from pure phenol on the one hand to pure camphor on the other, it will be possible to say, from the form of the curve, whether compounds of phenol and camphor are produced or not when the two substances are mixed.

The phenol used for the experiments was obtained from Kahlbaum, and was freed by distillation from any small amount of water which it might contain. The camphor was the best Japan variety. The results obtained from determinations of the melting points showed both substances to be quite pure.

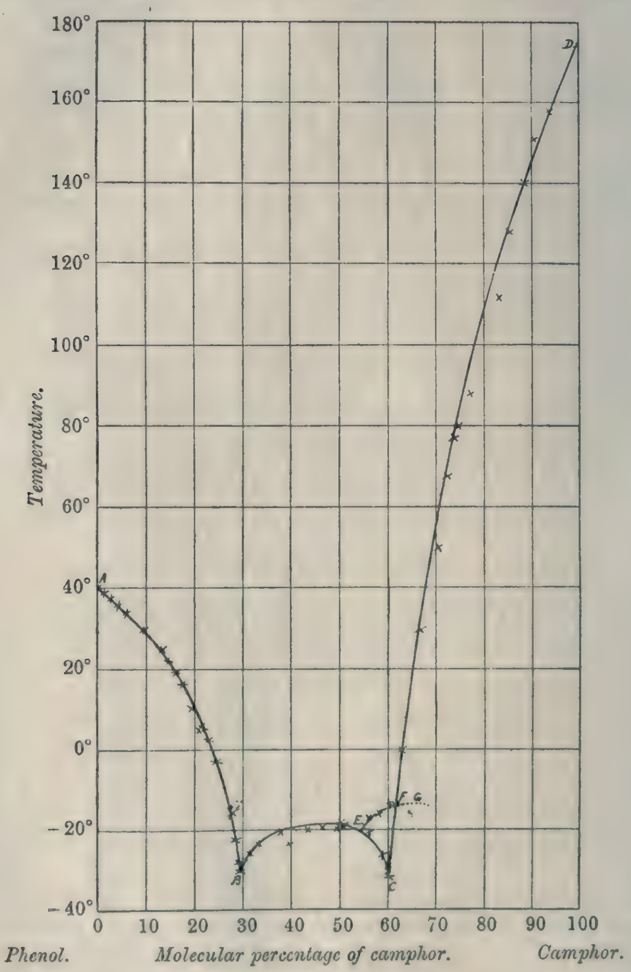
Suitable amounts of the two substances were weighed into a large test-tube, and were completely mixed by melting them together. The tube was then surrounded by a wider one, thus forming an air jacket, and the whole placed in a vessel filled with a suitable cooling medium. For the mixtures which contained only small amounts of camphor, water formed a suitable cooling agent, whilst in the case of mixtures in which only small quantities of phenol were present, the outer vessel was filled with hot mineral oil. For the cooling of the other mixtures, mixtures of ice and salt or of alcohol and solid carbon dioxide were employed. Uniformity of temperature in the mixture undergoing examination was secured in most cases by means of a mechanical stirring arrangement; with some of the mixtures stirring was difficult, because of the great viscosity of the mixture. Various thermometers were used to indicate the freezing point of the mixtures, a pentane thermometer being used to record the lowest temperatures. The different thermometers were compared with one another, and a table of corrections compiled, by means of which the readings given by different instruments could be made comparable. The commencement of freezing was quite apparent in the case of the mixtures containing small amounts of camphor, but with all other kinds of mixtures the most satisfactory way to detect the freezing point was found to be to measure the rate of cooling of the mixture, and note the point at which that rate changed. The change in the rate of cooling was in some cases of small dimensions, thus making it a matter of some difficulty to accurately determine the freezing point. It may also be mentioned that with those mixtures which contained large amounts of camphor, it was difficult to see when the camphor began to separate, owing to the refractive indices of the liquid and the solid being very nearly equal. On account of these difficulties, coupled with the difficulty of stirring already mentioned, many of the temperatures given in the table of results may be subject to an error which may amount to 1°. Several determinations of the freezing point were, as a rule, made with each mixture, the results of the different experiments being, for the most part, in close agreement when due allowance is made for the above-mentioned experimental difficulties.

In order to prevent the mixture from being too greatly undercooled, the consequence of which would, in all probability, be the

TABLE OF RESULTS.

Percentage of camphor in mixture.	Molecular percentage of camphor.	Freezing point.
0·00	0·00	40·3
2·32	1·44	39·0
4·53	2·85	37·5
6·87	4·36	36·1
9·42	6·04	34·2
14·86	9·75	29·7
20·31	13·61	25·0
21·64	14·59	22·0
24·10	16·42	19·0
25·40	17·40	16·1
28·52	19·79	10·5
28·92	20·10	7·9
30·31	21·19	5·0
32·64	23·05	2·4
34·50	24·57	−3·0
38·57	27·97	−15·7
39·52	28·78	−22·5
40·35	29·50	−28·0 −30·5
42·43	31·31	−25·7
44·90	33·51	−23·6
49·99	38·19	−20·4
52·52	39·88	−22·6
55·80	43·84	−20·0
58·73	46·80	−19·0
61·51	49·71	−20·1
62·21	50·46	−18·7
64·12	51·22	−19·0
66·64	55·28	−19·3
67·53	56·27	−16·7
67·74	56·48	−20·1
69·32	58·29	−15·9
70·12	59·21	−26·4 −32·0
71·48	60·78	−13·8
72·24	61·67	−13·5
73·37	63·02	−0·1
76·58	66·91	29·5
79·73	70·87	50·7
81·07	72·59	67·5
82·19	74·06	77·0
82·88	74·96	80·0
84·72	77·43	88·0
88·86	83·14	112·0
90·65	85·69	128·0
92·55	88·47	140·0
94·06	90·72	151·0
95·98	93·65	158·0
100·00	100·00	174·5

obtaining of too low values for the freezing points, the mixture was inocculated at a temperature near to that at which freezing was expected to take place with small amounts of phenol or camphor, according to which substance was separating out during freezing. The identity of the substance separating from any given mixture was established by filtering off a portion of the solid and, after thoroughly draining on porous tile, determining its melting point.



The curve showing the relation between the composition of the mixture and the freezing point is shown in the accompanying figure. It will be observed that the curve is made up of three distinct portions, namely, *AB*, *BC*, and *CD*; this fact indicates that the phenol and camphor actually combine to form a compound. The composition of this compound and its limits of stability are most readily seen by plotting, as has been done in the figure, the ratio between the number of molecules of each component in a given mixture instead of the relative weights of the two substances. On referring to the figure, it will be seen that the portion *BC*, which corresponds with the compound, reaches its greatest altitude at a point which corresponds with a molecular percentage of camphor of 50. Now the highest point of such a curve indicates the composition and freezing point of the pure compound; at this point the solid which separates and the liquid with which it is in contact have the same composition. It is obvious, therefore, that in the case of the compound of phenol and camphor, the two simple substances are united in equimolecular proportions, and that the freezing point of the compound is about −18·6°. The results of the authors' experiments confirm, therefore, the statement of Léger as to the existence of a monocamphoride of phenol, while the freezing point of the compound, as found by the authors, is in fairly close agreement with the melting point given by Léger.

When the two components are not present in equimolecular proportions, the freezing point of the mixture is lower than that of the pure compound, and falls towards *B* or *C* respectively, according as to whether it is phenol or camphor which is in excess. The points *B* and *C* are eutectic points, and represent the limits of stability of the compound. When the ratio between the molecular proportions of phenol and camphor exceeds that of 70·5 : 29·5, or falls below that of about 40 : 60, the compound can no longer exist in equilibrium with the liquid; in the former case, phenol will separate out when the mixture freezes, and in the latter case camphor. The lower freezing point given in the table of results for the mixtures containing molecular percentages of camphor of 29·5 and 59·21 represent the freezing points of the eutectic mixtures.

No indication was obtained by the authors as to the existence of a compound formed by the union of two molecules of phenol with one of camphor, as was stated to be the case by Léger; his statement as to the possibility of cooling the mixture to −50° without freezing taking place is in agreement with some of the authors' observations, they having noticed that mixtures in the neighbourhood of the eutectic point *B* can often be greatly supercooled without freezing ensuing.

It will be observed from the curve that two or three of the points in the neighbourhood of the eutectic point *C* do not fall on the curve. It might be considered that these points lie on another curve, shown by the dotted line in the figure; if such were the case it would show the existence of a second compound, the composition of which would be shown by the summit *G* of the curve, that is, a compound of two molecules of camphor with one of phenol. The authors do not take the latter view because of the quite definite eutectic point obtained with the 59·21 per cent. mixture, and because with mixtures having almost the same composition as those which gave the discordant results, figures were obtained which fall naturally on the portion *BC* of the curve. The points in question must therefore be considered as due to errors in the determination of the freezing point, probably arising from one or other of the causes mentioned in the earlier part of the paper.

University College,
Dundee.

CXLVII.—*Morphological Studies of Benzene Derivatives. Part I. Introductory.**

By Henry E. Armstrong.

In this series of communications a description will be given of the results of an inquiry which has been carried on in the laboratory under my charge at the City and Guilds Central Technical College, during many years past, whenever I could secure the assistance of competent workers. A brief reference to the work which gave rise to it is to be found in the *Proceedings* of March 3rd, 1892 (p. 40), under the title, "*The Relative Orienting Effect of Chlorine and Bromine. I.—The Constitution of Parabrom- and Parachloranilinesulphonic Acids*" by Henry E. Armstrong and J. F. Briggs.

With the object of ascertaining whether any difference in the orienting influence of the two halogen elements could be detected, we had sulphonated *p*-chlorobromobenzene: the product appeared to be a single substance; the results we obtained on contrasting it with the sulphonic acids prepared from *p*-chlor- and *p*-bromanilinesulphonic acids respectively also led us to assume that the sulphonic radicle occupied the ortho-position relatively to the chlorine atom.

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* In this and the following paper the authors have not always used the nomenclature adopted by the Publication Committee of the Chemical Society: for example, they prefer "ethylic salt" to "ethyl ester."

In view of the fact that corresponding chloro- and bromo-derivatives differ but very slightly in general behaviour, however, the apparently exclusive attraction of the sulphonic radicle by chlorine rather than by bromine was more than surprising; the subject was therefore made the object of further study.

In 1895, with the assistance of Mr. W. T. Gidden, an exhaustive examination was made of the acids obtained on sulphonating *p*-chlor- and *p*-brom-aniline under various conditions. Mr. Briggs, following the directions given by Claus and Mann (*Annalen*, 1891, **265**, 87), had mixed the aniline sulphate with eight times its weight of an acid containing 15 per cent. of anhydride and heated the mixture on the water-bath during four hours. In each case only the *meta-acid* was isolated.*

Little was known at the time of the ortho-acids. Various methods of preparing these were tried. A mixture of *p*-brom-aniline sulphate with a molecular proportion of sulphuric acid (100 per cent. acid) was heated at 200—220° during three hours; the ortho-acid only was formed but the yield was very small. Better results were obtained by Limpricht's method—by heating the sulphonate at about 200°. At about this time Kreis described a method of preparing the ortho-acid (*Annalen*, 1895, **286**, 377), which involved heating rapidly, in an open dish, a mixture of *p*-bromacetanilide and an equivalent proportion of ordinary concentrated sulphuric acid until the acetic acid was expelled, then baking the salt in an air-oven at 180°. This method was found to give excellent results and to be equally applicable to *p*-chloracetanilide, only the ortho-acid being formed.

The fact that on heating the sulphate with a large excess of fuming acid it was converted into the meta-acid, whilst the ortho-acid was produced when only a single molecular proportion of sulphuric acid was used, called for an explanation; it appeared not improbable that the meta-acid might have been formed by the conversion of the ortho-mono-acid produced at first into an unstable ortho-meta-disulphonic acid, which was subsequently deprived of its ortho-sulphonic radicle. On sulphonation, however, the ortho-mono-sulphonic acid gave rise only to a diortho-disulphonic acid: it was therefore to be supposed that the ortho- and meta-acids were products of distinctly different operations. This observation led me to institute a general inquiry into the process of sulphonation: of this only brief accounts have been published (compare Proc., 1900, **16**, 159; *Brit. Assoc. Report*, Dover, 1899, p. 683). I hope to bring the work under the notice of the Society at an early date, partly in connexion with the chemical side of the inquiry now under consideration and in further discussion of the "laws" which govern substitution in benzenoid compounds.

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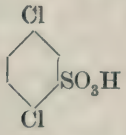
* Later observations show that, on sulphonating *p*-chlor- and *p*-brom-acetanilide with fuming acid, a small proportion of ortho-acid is also formed; whether this be the case when the sulphate is used is now being ascertained.

Two isomeric *p*-chlorobromobenzenesulphonic acids were obtained from the two isomeric *p*-chloraniline- and also from the *p*-bromaniline-*o*- and -*m*-sulphonic acids, corresponding pairs of the amino-acids yielding isomeric acids when the amino-radicle was displaced by halogen. The sulphonic chloride of the one chlorobromosulphonic acid melted at 66°, that of the other at 46°; mixtures of the two melted at intermediate temperatures, the melting point varying as the composition of the mixture was varied according to a linear law: the behaviour of the two compounds, in fact, was in all respects that of isomorphous substances.

The product obtained on sulphonating *p*-chlorobromobenzene gave a sulphonic chloride melting at about the temperature of a mixture of equal proportions of the two sulphonic chlorides; numerous attempts were made to separate the two acids of which it undoubtedly consisted by fractionally crystallising various salts and other derivatives but these were all unsuccessful.

The mistake Mr. Briggs and I had made in assuming that only a single acid was formed was admitted in a note communicated to the British Association at Dover in 1899 (*Report*, p. 687).

I determined to extend the inquiry on the crystallographic side, with the help of Mr. Gidden, to the complete series of sulphonic chlorides and bromides derivable from the *p*-dichloro-, *p*-dibromo- and *p*-chlorobromo-benzenesulphonic acids represented by the formulæ:



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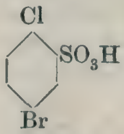

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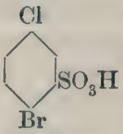

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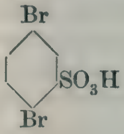


(IV.)

We were able to prepare five of the eight allied compounds in measurable form but were unable to obtain satisfactory crystals of the chloride of both I and III and did not succeed even in preparing the bromide of the latter. The five compounds measured proved to be strictly isomorphous and no indication of polymorphism was observed during their examination; it was found, however, that the ethylic salt prepared from II stood in close morphotropic relationship with the chlorides but was not isomorphous with them. The chlorides and bromides all crystallised in the monosymmetric system, the ethylic salt in the orthorhombic. The following data obtained at this time show how small were the differences observed between the various compounds and particularly that less alteration in crystalline form is involved in the change from sulphonic chloride to bromide than is produced by substituting chlorine for bromine in the benzene nucleus.

Geometrical Constants.

	Axial ratios.	Angle.	Angle $110 : 1\bar{1}0$.
$Cl : Br : SO_2Cl = 1 : 4 : 2$	1·1778 : 1 : 2·6216	108°44′23″	96°15′
$Cl : Br : SO_2Br = 1 : 4 : 2$	1·1708 : 1 : 2·6250	107 35 21	96 17
$Br : Br : SO_2Cl = 1 : 4 : 2$	1·1456 : 1 : 2·6331	110 20 26	94 6
$Br : Br : SO_2Br = 1 : 4 : 2$	1·1516 : 1 : 2·6635	109 6 43	94 50
$Cl : Cl : SO_2Br = 1 : 4 : 2$	1·1664 : 1 : 2·5861	107 47 42	96 0

In communicating our results to the British Association at Dover (1899), I stated that I had formed the plan of extending the inquiry to the 1 : 3- and 1 : 2-di-derivatives of benzene containing halogens. I was able to announce that Dr. E. C. Jee had already measured the compounds of the 1 : 3 : 4-series and had discovered that they formed a remarkable *isotrimorphous* group bearing no apparent relationship to the para-series.

The following year (1900) at Bradford, it was stated in the First Report of the Committee on Isomorphous Derivatives of Benzene (p. 167) that the series included anorthic, orthorhombic and monosymmetric terms, as shown in the following table:

	Orientation.			Crystallographic system.				
No.	1.	3.	4.	Anorthic.		Orthorhombic.		Monosymmetric.
1	Cl	Cl	SO_2Br	stable				
2	Cl	Br	SO_2Br	stable				
3	Br	Cl	SO_2Br	stable				
4	Br	Br	SO_2Br	labile	→	stable		
5	Br	Br	SO_2Cl	(labile)	→	stable		labile
6	Br	Cl	SO_2Cl			stable		labile
7	Cl	Br	SO_2Cl			labile	→	stable
8	Cl	Cl	SO_2Cl			labile	→	stable

Of these eight substances, it was pointed out, three are stable in the anorthic system, three in the orthorhombic system and two in the monosymmetric system. Change of the one form into the other had been observed in four cases (4, 5, 7, 8) on allowing the fused substance to cool on a microscopic slide, the direction of the change in each case being that indicated in the table by an arrow. A labile anorthic form of dibromobenzenesulphonic bromide (4) had been crystallised out from solution; moreover, it had been found that each of the four sulphonic chlorides (5—8) can be caused to crystallise in the alternative system by admixture with a sulphonic chloride which usually separates in that system. It had been possible to determine the symmetry of all the forms referred to in the table by crystallographic measurement, with the single exception of the labile anorthic form of dibromobenzenesulphonic chloride but the existence of this form was indicated by the dimorphous change which occurs on cooling from the melting point to atmospheric temperature.

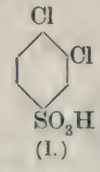
In 1902, at Belfast, I was able to report that Dr. Jee had also practically completed the examination of the second of the three series of 1 : 3-derivatives (the 1 : 3 : 5-sulphonic series) and that these constituted an *isotetramorphous* group, as shown in the following table:

	Orientation.			Crystallographic systems.			
No.	1.	3.	5.	Anorthic.	Mono-symmetric.	Mono-symmetric.	Anorthic.
1	Cl	Cl	SO_2Br	stable	stable		
2	Cl	Br	SO_2Br		stable		
3	Br	Br	SO_2Br		stable	labile	
4	Br	Br	SO_2Cl			stable	
5	Br	Cl	SO_2Cl			stable	
6	Cl	Cl	SO_2Cl				stable

In this series also the dibromobenzenesulphonic bromide is the means of establishing the relationships between the various terms, having been obtained in two distinct forms. But in comparison with the 1 : 3 : 4-series, the order of stability is reversed, the transition temperature becoming lower in passing down the series.

The third 1 : 3(2 sulphonic)-series has given the greatest trouble and up to the present time I have succeeded in obtaining only one of its terms.

In the case of the 1 : 2-series, five of the eight terms of the 1 : 2 : 4-series have been measured by Mr. H. Harding, namely, the chlorides derived from acids I, II and IV and the bromide of II:



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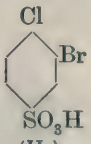

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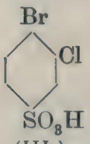

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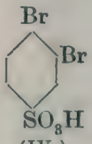

(IV.)

Of the chlorides, I and II are practically identical in form; the chloride of IV has been obtained in a distinct form, belonging, however, to the same crystalline system as I. The bromide of II has been obtained in both forms, so that it establishes a connecting link between the two isomorphous series which evidently exist. In this series, the measurements are made with particular difficulty, owing to the low melting points of the compounds and their marked tendency to crystallise in very thin, micaceous plates. Several anilides of this series have been examined and found to exist in two forms.

The difficulties connected with the preparation of the second 1 : 2-series [the 1 : 2(3 sulphonic)-derivatives] are not yet overcome.

In planning the inquiry, I hoped that it would be possible eventually to deduce from the data obtained definite conclusions permitting of the correlation of external form with internal molecular structure. The regular relationships discovered in the course of the work served to justify this expectation but there was no obvious mode of discussing the data with such an object in view. I hesitated to publish results which I could not interpret in some definite manner. At this juncture the masterly memoir of Barlow and Pope was published, connecting crystalline form with molecular configuration; hope arose in my mind that it would be possible to interpret our data in the light of their views.

It appeared desirable to deal first with the 1 : 4-series, in which the simplest relationships prevailed between individual members. I was fortunate in securing the assistance of two of my students, Messrs. Colgate and Rodd. With their aid, the earlier work has been revised and the series extended, so as to include the 1 : 4-iodo- as well as the chloro- and bromo-derivatives and a variety of sulphonates—ethereal salts and simple and substituted amides—twenty-nine in all. The results at which they have arrived, described in the following memoir, appear to afford clear proof of the existence of a *benzene framework* in all the molecules; it would seem therefore, taking also into account the results previously arrived at by Jerusalem in the case of certain nitro-compounds, that the scheme put forward by Barlow and Pope is one which will embrace the benzenoid compounds generally.

Dr. Jee's and Mr. Harding's measurements of compounds of the 1 : 3- and 1 : 2-series will be described and discussed in later communications; the conclusions that can be deduced from them appear to be similar to those arrived at in the case of the 1 : 4-compounds.

A clue having been found, I hope at no distant date to complete the task which I have undertaken and that it will then be possible to discuss and define the manner in which the superstructure is erected upon the benzene framework. The material collected will also need discussion in other directions.

When the series is completed, if only the sulphonic chlorides and bromides of the dichloro-, dibromo- and bromochloro-benzenes are measured, forty-four different types of compound will have been examined. Thirty of these have been measured already. We shall then have ascertained the angles, so to speak, of almost every possible facet that can be developed on the benzene molecule. If, as appears to be probable, a substructure of benzene be always revealed, whatever the nature of the compound, the proof will be compete that the structural elements preserve their individuality in the molecule. To have arrived at such a result will be more than ample reward for the large amount of time and labour spent on the inquiry. Those engaged in the study of constitution have long been satisfied that they are dealing with realities and that the formulæ in which they have expressed their conclusions must be given actual value. Structural formulæ, however, are as much symbolic of function as of the relative arrangement of the parts; that it should be possible to go further and define the position of these parts in space and the geometrical outcome of their arrangement is a remarkable achievement in which chemists may well take pride.

I would urge in conclusion that the value of crystallography to the chemist should be more fully recognised. The discipline the study affords is in itself of very great value. But it is only right that the chemist should understand and be able to use the language in which alone the crystalline substances he prepares can be described. Analysis is not a means of defining any particular substance; but if crystalline form be determined, a substance is defined for all time and can always be recognised.

The early stages of this work were carried out with the assistance of Mr. Pope, then Instructor of Crystallography in our College; later workers have been aided by Dr. Lowry, his successor. I have to thank both these gentlemen. We are also greatly indebted to Prof. Pope for the aid he has given us in our recent discussion of the data. I have also to acknowledge the help I have received from the Government Grant Fund of the Royal Society and from the British Association.

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CXLVIII.—*Morphological Studies of Benzene Derivatives. Part II. Sulphonic Derivatives of the 1 : 4-Di-derivatives of Benzene containing Halogens.*

By REGINALD THOMAS COLGATE and ERNEST HARRY RODD.

NINE sulphonic acids of benzene are possible containing two halogen atoms—either chlorine, bromine or iodine—in the para-position in the nucleus; simpler derivatives of all of these have been prepared and have been subjected to careful goniometric examination. The axial ratios and other quantities connected therewith are stated in the table on p. 1590. All the compounds examined crystallise in the monosymmetric system, excepting those numbered 28 and 29, which are orthorhombic.

The nine possible sulphonic chlorides have all been obtained in a form suitable for measurement but several of the corresponding bromides have not yet been isolated, as difficulties attend their preparation; all that have been examined fall into one or other of two crystallographic groups; in each of these groups the individual members have similar geometrical constants and are similar in habit and general crystalline form. The first group includes the substances numbered 1 to 12 in the table; the second comprises substances 13, 14 and 15. It is noteworthy that each series includes one of the isomeric chloriodobenzenesulphonic chlorides but that the sulphonic bromide of the 1 : 4 : 2-sulphonic acid occurs in the same series as the chloride of the isomeric 1 : 4 : 3-acid. This behaviour is an indication of isodimorphism, and on one occasion a crop of crystals of a labile modification of the 1 : 4-iodochlorobenzene-2-sulphonic chloride was actually obtained: these crystals rapidly became cloudy and opaque after removal from the benzene solution but melted at 70°, the melting point of the stable form. Apparently the labile form can be obtained by suddenly cooling the molten substance, as when thus treated the compound melts at 62°. In the case of 1 : 4-bromoiodobenzene-2-sulphonic chloride, not only was a similar crop of labile crystals obtained but it was found possible to measure it. The result showed clearly that the modification belongs to the first or large group; the stable modification, which we have not yet obtained in measurable form, is presumably a member of the second group.

Although the axial ratios of the members of the two series are widely different, on comparing their equivalence parameters it is obvious that the substances are closely related.*

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* As defined by Barlow and Pope, the equivalence parameters represent the dimensions of a parallelopipedon the edges of which are parallel with and pro-

Barlow and Pope have shown that two alternative modes exist of close-packing the benzene units or molecules in homogeneous arrangement (Trans., 1906, **89**, 1699); these are derived respectively from the hexagonal and the cubic closest-packed arrangement of equal spheres. The former type of arrangement is exhibited in the known orthorhombic modification of benzene, which has the axial ratios $a:b:c=0{\cdot}891:1:0{\cdot}799$, Barlow and Pope having shown clearly that these constants are obtainable by a slight distortion of the completely hexagonal mode of packing the benzene units; this arrangement is known as the hexagonal marshalling of the benzene units. Calculating from these axial ratios and taking into account the valency volume of the hydrocarbon ($W=30$), the equivalence parameters of this type of marshalling of the benzene assemblage are $x:y:z=3{\cdot}101:3{\cdot}480:2{\cdot}780$. These numbers represent translations in the crystalline benzene assemblage in three directions at right angles; on inspection of the Barlow-Pope diagrams, it is obvious that the value $z=2{\cdot}780$ is a measure of the height of two links in the column of carbon spheres in the assemblage. Whilst the diagrams represent the z value as being very slightly less than the sum of the diameters of one carbon and one hydrogen domain, the quantity $y=3{\cdot}480$ is twice the diameter of a carbon domain. These quantities refer to dimensions in the assemblage after suppression of the interstitial space. It has been shown by Barlow and Pope and by Jerusalem that the dimension $z=2{\cdot}780$ occurs as one of the equivalence parameters in a large number of benzene derivatives which have been crystallographically examined and it has been concluded that when hydrogen atoms in the benzene molecule are displaced by other atoms or radicles, the columns of carbon spheres in the crystalline assemblage referred to above retain their structure intact and are merely moved apart to accommodate the substituting groups.

The alternative mode of close-packing the benzene units in homogeneous assemblage is derived from the cubic closest-packed assemblage of equal spheres; in this type of assemblage the z dimension must be rather smaller than in that previously considered. As this assemblage presents a rhombohedral form of arrangement, it is termed the rhombohedral marshalling of the benzene units. The marshalling being rhombohedral, crystals affecting this type of structure must be expected to exhibit (*a*) pseudo-hexagonal symmetry, one of the axial ratios approximating to $1:1{\cdot}1547$ or $1:0{\cdot}8165$; on the other hand,

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portional to the crystallographic axes, its volume being numerically equal to the sum of the fundamental valencies of the atoms in the molecule. The equivalence parameters of the substances described are calculated in the case of compounds 1 to 15 from the axial ratios deduced from the actual measurements, no fractional parts of the axial ratios being used.

being derived from the cubic closest-packed assemblage of equal spheres, it may also show (*b*) pseudo-cubic symmetry. In the case of (*a*), one of the equivalence parameters should have a value somewhat less than 2·78, whilst in the case of (*b*) the value somewhat less than 2·788 cannot appear but either two or the three equivalence parameters should be nearly equal.

Jerusalem has shown clearly that the anticipations expressed above, which are summarised from Barlow and Pope's description (*loc. cit.*, p. 1692), are realised in the results obtained by the crystallographic examination of the picrates and styphnates (Jerusalem, Trans., 1909, **95**, 1275).

Inspection of the equivalence parameters of the sulphonic chlorides and bromides recorded in the table on p. 1590 shows that with the exception of No. 13 all include a z value appreciably less than 2·780; the values lie between 2·661 and 2·741, the total variation being about 3 per cent.

Further, in Nos. 1 to 12 the ratio $c:b$ approximates to the hexagonal ratio of 1·1547 : 1; in Nos. 13 to 15 the ratio $a:b$ approximates, although less closely, to the alternative hexagonal ratio of 0·8165 : 1. There is thus considerable evidence that all these substances are of the rhombohedral type of marshalling, with the possible exception of No. 12, in which the z value is nearly appropriate to the hexagonal marshalling. The considerable difference between the β-angle for No. 13 and those for Nos. 14 and 15 confirms the suggestion that both types of marshalling occur in the three substances. Another point of interest in connexion with the equivalence parameters is that when it is possible to compare the numbers for corresponding sulphonic chlorides and bromides, as in pairs 1 and 2, 3 and 4, 7 and 8, 10 and 11, the y parameters are nearly identical; the morphotropic relationship thus displayed, however, is only revealed by the equivalence parameters.

We have determined the axial ratios and equivalence parameters of a considerable number of sulphanilides and sulphotoluidides derived from the chlorides. Most of these substances crystallise far more readily than the chlorides and bromides in measurable form and may therefore be measured accurately with facility. The equivalence parameters deduced for these substances are such that they must be supposed to exhibit one or other of the two kinds of marshalling already discussed.

The anilides and toluidides are in several cases isodimorphous. Pure *p*-dibromobenzenesulphanilide, for example, crystallises from acetone in a labile form; when removed from the solution, the crystals are brilliant and transparent but almost immediately become opaque and the crystal faces dull; the measurement of this compound was therefore a matter of some difficulty. It appears that the presence of a trace of aniline in the solution always ensures the deposition of the compound in the stable form.

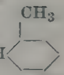
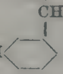
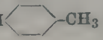
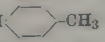
1 : 4-Chlorobromobenzene-2-sulphanilide is another similar case. Only a few measurements of the labile form of this compound were obtained but judging from these and from the forms appearing on the crystals it is closely isomorphous with the labile form of *p*-dibromobenzenesulphanilide. All the other anilides studied up to the present have been obtained as yet only in a stable form. The following data have been deduced from the measurements made of the anilides:

	Orientation.						
	1.	4.	2.	*a* : *b* : *c*.	β.	*x* : *y* : *z*.	M. p.
17	Cl	Br	SO_2·NHPh	1·339 : 1 : 1·058	98° 7′	7·752 : 2·894 : 3·062	138°
18	Br	Cl	SO_2·NHPh	1·338 : 1 : 1·047	98 30	7·776 : 2·906 : 3·043	164
19	Br	Br	SO_2·NHPh	1·329 : 1 : 1·025	97 58	7·793 : 2·932 : 3·005	143
20	I	Cl	SO_2·NHPh	1·350 : 1 : 0·997	97 15	7·943 : 2·942 : 2·933	168
21	I	Br	SO_2·NHPh	1·329 : 1 : 0·979	97 18	7·909 : 2·976 : 2·913	150
22	Br	Br	SO_2·NHPh	1·372 : 1 : 1·163	97 50	7·631 : 2·781 : 3·234	143

The valency volume of the anilides is 68; the parameter values are obtained by multiplying the *a* axial ratio value by 28. These anilides evidently constitute a well-defined isomorphous group. The fact that a number approximating to 2·9 occurs twice in each set of equivalence parameters is an indication that in each case the axial directions have been so chosen as to demonstrate the pseudo-cubic nature of the assemblage, a possibility which we have already considered. The property of exhibiting pseudo-cubic symmetry being characteristic of the rhombohedral type of marshalling of benzene units, we conclude that the anilides display that type of marshalling in their crystals. The compound numbered 22 is the labile form of *p*-dibromobenzenesulphanilide. Its crystals evidently display hexagonal marshalling, as the number 2·78 occurs among the parameter values. The labile form of 1 : 4-chlorobromobenzene-2-sulphanilide (17) we have proved to be isomorphous with (22), although we have not been able to measure it completely.

It is clear from the evidence that the sulphanilides form an isodimorphous group of substances, as each of two of the compounds has been obtained in two forms, one stable and the other labile, the two stable forms and the two labile forms being respectively isomorphous. As the stable crystals exhibit rhombohedral and the labile hexagonal marshalling, both types of arrangement characteristic of benzene are represented in this group of compounds.

To contrast the toluidides with the anilides, we have prepared and measured the *o*-, *m*- and *p*-toluidides of 1 : 4-chlorobromobenzene-2-sulphonic acid and also the *p*-toluidide of *p*-dibromobenzenesulphonic acid. The results obtained are as follows:

	Orientation.						Fractions	
	1.	4.	2.	$a : b : c$.	β.	$x : y : z$.	of ratios.	M. p.
20	Cl	Br	$SO_2 \cdot NH$ 	0·727 : 1 : 1·195	102° 5′	8·122 : 2·792 : 3·262	4a	151°
21	Cl	Br	$SO_2 \cdot NH$ 	0·751 : 1 : 1·154	100 37	8·430 : 2·782 : 3·210	4a	159·5
22	Cl	Br	$SO_2 \cdot NH$ 	0·767 : 1 : 0·959	98 25	9·022 : 2·940 : 2·820	4a	157
23	Br	Br	$SO_2 \cdot NH$ 	0 764 : 1 : 0·959	98 32	9·001 : 2·943 : 2·824	4a	152

A striking fact is disclosed in these results: the *o*- and *m*-toluidides are obviously derived from the labile anilide, being of hexagonal marshalling, as the presence among the parameters of the number 2·78 indicates; the *p*-toluidide, on the other hand, is clearly derived from the stable anilide, being of rhombohedral marshalling and exhibiting pseudo-cubic symmetry.

The following comparison gives emphasis to these relationships:

	$x : y : z$.		$x : y : z$.
Labile anilide (19)	7·631 : 2·781 : 3·234	Stable anilide (14)	7·752 : 2·894 : 3·062
o-Toluidide (20) ..	8·122 : 2·792 : 3·262	Stable anilide (16)	7·793 : 2·932 : 3·005
m-Toluidide (21) ...	8·430 : 2·782 : 3 210	*p*-Toluidide (22) ...	9·022 : 2·940 : 2·820
		p-Toluidide (23) ...	9·001 : 2·943 : 2 824

The greater part of the change of the dimensions conditioned by the introduction of a methyl group in place of an atom of hydrogen occurs in one direction, namely, on the x parameter.

Indications of dimorphism have been observed in the case of the *o*-toluidide (20). The melting point of crystals separated from acetone is 151°. If the melted substance be suddenly cooled, however, it assumes the vitreous or isotropic state but when gently warmed the solid crystallises in a form which melts at 142—143°.

It is clear from the occurrence of the value 2·78 in the equivalence parameters of the anilides and toluidides that in these compounds the two benzene nuclei must lie in the same plane. Barlow and Pope have shown this to be the case in other compounds containing more than one benzene nucleus, for example, in triphenylmethane.

We have also prepared the methylic and ethylic salts of *p*-dibromobenzenesulphonic acid and the ethylic salt of 1 : 4-chloroiodobenzene-2-sulphonic acid. The two ethylic salts crystallise in the orthorhombic and the methylic in the monosymmetric system. All were obtained in measurable form only after considerable trouble.

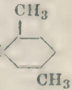
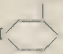
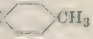
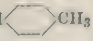
The following results were obtained:

Orientation.					Fractions		
1.	4.	2.	$a : b : c$.	W.	of ratios.	$x : y : z$.	β.
Br	Br	$SO_2 \cdot OMe$	2·443 : 1 : 1·167	44	—	5·995 : 2·454 : 2·930	94°0′
Br	Br	$SO_2 \cdot OEt$	1·197 : 1 : 1·065	50	2a	6·455 : 2·697 : 2·872	90 0
I	Cl	$SO_2 \cdot OEt$	1·294 : 1 : 1·114	50	2a	6·697 : 2·589 : 2·883	90 0

The *y* parameter values may be regarded as indicating that these compounds are of rhombohedral marshalling, the *y* value being somewhat less than the $z = 2{\cdot}78$ value characteristic of benzene.

To sum up, it is apparent that all the compounds described in the present communication are of two types, one derived from the hexagonal and the other from the cubic mode of packing equal spheres in the closest possible manner.

It is to be supposed that the carbon atoms in each molecular complex are arranged in almost exactly the same manner as are those in crystalline benzene and that the substituting atoms or groups take the place of the hydrogen atoms they displace by expanding the benzene assemblage in two only of the three possible directions. The orthorhombic symmetry of the benzene assemblage is usually lowered, however, to monosymmetric symmetry, the shear which causes this change taking place in a direction parallel with either plane of symmetry of the orthorhombic assemblage, so that the value 2·78 is found on either the *y* or the *z* parameter in the monosymmetric derivative; thus in the case of 1 : 4-chloroiodobenzene-2-sulphonic chloride this

	Orientation.			Axial ratios.			Equivalence parameters.	
	1.	2.	4.	*a* : *b* : *c*.	β.	*W*.	*x* : *y* : *z*.	M. p.
1	Cl	SO_2Cl	Cl	2·450 : 1 : 1·179	97°25′	36	5·696 : 2·325 : 2·741	38°
2	Cl	SO_2Br	Cl	2·490 : 1 : 1·166	98 41	36	5·785 : 2·323 : 2·709	74
3	Cl	SO_2Cl	Br	2·509 : 1 : 1·178	97 40	36	5·790 : 2·308 : 2·718	66
4	Cl	SO_2Br	Br	2·531 : 1 : 1·171	98 35	36	5·840 : 2·307 : 2·702	110
5	Br	SO_2Cl	Cl	2·398 : 1 : 1·133	96 5		5·685 : 2·370 : 2·687	46
6	Br	SO_2Br	Cl	2·438 : 1 : 1·145	97 45	36	5·735 : 2·352 : 2·693	83
7	Br	SO_2Cl	Br	2·476 : 1 : 1·144	95 26	36	5·787 : 2·337 : 2·674	71
8	Br	SO_2Br	Br	2·479 : 1 : 1·145	96 49	36	5 796 : 2·338 : 2·676	114
9	I	SO_2Br	Cl	2·469 : 1 : 1·154	95 50	36	5·761 : 2·333 : 2·692	102
10	Cl	SO_2Cl	I	2·583 : 1 : 1·176	99 7	36	5·914 : 2·289 : 2·692	88
11	Cl	SO_2Br	I	2·567 : 1 : 1·167	100 30	36	5·912 : 2·303 : 2·689	143
12	Br	SO_2Cl	I	2·555 : 1 : 1·158	94 23	36	5·882 : 2·302 : 2 666	91
13	I	SO_2Cl	Cl	0·729 : 1 : 0·654	99 42	36	3·095 : 4·247 : 2·779	70
14	I	SO_2Cl	Br	0·815 : 1 : 0·673	95 28	36	3·291 : 4·040 : 2·719	97
15	I	SO_2Cl	I	0·885 : 1 : 0·668	95 22	36	3·409 : 3·986 : 2·661	132
16	Cl	SO_2·NH_2	Cl	0·423 : 1 : 0·421	91 44		2·573 : 6·079 : 2·558	182
17	Cl	SO_2·NHPh	Br	1·339 : 1 : 1·058	98 7	68	7·752 : 2·894 : 3·062	138
18	Br	SO_2·NHPh	Cl	1·338 : 1 : 1·047	98 30	68	7·776 : 2·906 : 3·043	164
19	Br	SO_2·NHPh	Br	1·329 : 1 : 1·025	97 58	68	7·793 : 2·932 : 3·005	143
20	I	SO_2·NHPh	Cl	1·350 : 1 : 0·997	97 15	68	7·943 : 2·942 : 2·933	168
21	I	SO_2·NHPh	Br	1·329 : 1 : 0·979	97 18	68	7·909 : 2·976 : 2·913	150
*22	Br	SO_2·NHPh	Br	1·372 : 1 : 1·163	97 50	68	7·631 : 2·781 : 3·234	143
23	Cl	SO_2·NH 	Br	0·727 : 1 : 1·195	102 5	74	8·122 : 2·792 : 3·262	151
24	Cl	SO_2·NH 	Br	0·751 : 1 : 1·154	100 37	74	8·430 : 2·782 : 3·210	159
25	Cl	SO_2·NH 	Br	0·767 : 1 : 0·959	98 25	74	9·022 : 2·940 : 2·820	157
26	Br	SO_2·NH 	Br	0·764 : 1 : 0·959	98 32	74	9·001 : 2·943 : 2·824	152
27	Br	SO_3Me	Br	2·443 : 1 : 1·167	94 0	44	5·995 : 2·454 : 2·950	63
28	Br	SO_3Et	Br	1·197 : 1 : 1·065	90 0	50	6·455 : 2·697 : 2·872	106
29	I	SO_3Et	Cl	1·294 : 1 : 1·114	90 0	50	6·697 : 2·589 : 2·888	88

* Labile form.

number is found on the z parameter, whilst in that of the labile *p*-dibromobenzenesulphanilide it occurs on the y parameter.

The halogen atoms appear to displace one another in the molecule without producing more than a slight change in the relative dimensions of the structure.

The preceding is a complete list of the compounds described:

1. p-*Dichlorobenzenesulphonic Chloride.*

Great difficulty was experienced in obtaining this substance in measurable crystals. Until highly purified, it did not crystallise at all, the solution solidifying as a whole when very concentrated. Measurable crystals (m. p. 38°) were at length obtained from a solution in benzene kept at the temperature of melting ice. [Found, (sulphonic) Cl = 14·43. Calc., Cl = 14·46 per cent.]

System: Monosymmetric.
Axial Ratios: $a : b : c = 2{\cdot}450 : 1 : 1{\cdot}179$; $\beta = 97°25'$.
Equivalence Parameters: $x : y : z = 5{\cdot}696 : 2{\cdot}325 : 2{\cdot}741$.
Forms observed: $\{100\}$, $\{111\}$, $\{001\}$, $\{110\}$, $\{\bar{1}11\}$, $\{221\}$.

The following measurements were made:

Angle.	No. of observations.	Limits.	Mean.	Calculated.
$100 : 110$	19	67°22′—67°58′	67°38′	—
$110 : \bar{1}10$	9	44 35 —45 3	44 45	44°44′
$100 : 111$	15	76 35 —77 33	77 5	—
$111 : \bar{1}11$	8	34 9 —35 8	34 34	34 37
$\bar{1}11 : \bar{1}00$	7	68 18 —68 23	68 19	68 18
$001 : 111$	6	53 11 —53 25	53 16	53 23
$111 : 110$	2	39 14 —39 35	39 23	39 26
$001 : \bar{1}11$	2	49°47′	49 47	49 56
$100 : 001$	5	97 22 —97 28	97 25	—
$001 : \bar{1}00$	5	82 30 —82 34	82 33	82 34
$111 : 1\bar{1}1$	2	95 47 —95 51	95 49	96 2

2. p-*Dichlorobenzenesulphonic Bromide.*

This substance was prepared and measured by Gidden. The axial ratios given by him were recalculated for a different value of β. His data with corrected indices for the faces are given below. Melting point 74°:

Axial Ratios: $a : b : c = 2{\cdot}490 : 1 : 1{\cdot}166$; $\beta = 98°41'$.
Equivalence Parameters: $x : y : z = 5{\cdot}785 : 2{\cdot}323 : 2{\cdot}709$.

Angle.	No. of observations.	Mean.	Calculated.
$111 : 1\bar{1}1$	41	96° 0′	—
$100 : 111$	63	78 12	—
$100 : 00\bar{1}$	10	81 19	—
$111 : 001$	10	53 14	53°12′
$100 : 110$	4	67 53	67 54
$111 : \bar{1}10$	2	52 20	52 18

5. 1 : 4-*Bromochlorobenzene-2-sulphonic Chloride.*

In preparing this compound, even more difficulty was experienced in crystallising it than in the case of *p*-dichlorobenzenesulphonic chloride. From benzene or a mixture of benzene and light petroleum, it separates in very thin, hexagonal plates melting at 46°; by keeping the solution at 0°, thicker crystals are obtained but their laminated structure renders them useless for purposes of measurement; ultimately measurable crystals were obtained from a mixture of benzene with petroleum boiling at 100—120°. [Found, (sulphonic) Cl = 12·17. $C_6H_3O_2Cl_2Br$ requires (sulphonic) Cl = 12·23 per cent.]

System: Monosymmetric.

Axial Ratios: $a : b : c = 2{\cdot}398 : 1 : 1{\cdot}133$; $\beta = 96°5'$.

Equivalence Parameters: $x : y : z = 5{\cdot}685 : 2{\cdot}370 : 2{\cdot}687$.

Forms observed: {100}, {001}, {110}, {111}, {22$\bar{1}$}.

The following measurements were made:

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100 : 111	13	76° 5′— 76°38′	76°18′	—
111 : $\bar{1}$00	11	103 27 —103 51	103 41	103°42′
100 : 001	11	95 29 — 96 25	96 1	96 5
001 : $\bar{1}$00	12	83 30 — 84 29	83 55	—
001 : 111	15	51 30 — 52 27	52 7	—
111 : 110	2	40 4 — 40 13	40 9	40 15
111 : 22$\bar{1}$	4	61 43 — 62 19	61 55	61 59
22$\bar{1}$: 00$\bar{1}$	2	65 32 — 65 48	65 40	65 54
100 : 22$\bar{1}$	3	66 40 — 67 16	66 55	66 54

6. 1 : 4-*Bromochlorobenzene-2-sulphonic Bromide.*

This compound was measured by H. Harding; it melts at 83°.

System: Monosymmetric.

Axial Ratios: $a : b : c = 2{\cdot}4383 : 1 : 1{\cdot}1456$; $\beta = 97°45'$.

Equivalence Parameters: $x : y : z = 5{\cdot}735 : 2{\cdot}352 : 2{\cdot}693$.

Forms observed: {100}, {001}, {111}.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100 : 001	8	82° 2′—82°38′	82°15′	—
100 : 00$\bar{1}$	5	97 34 —97 48	97 45	97 45
001 : 111	4	52 37 —52 42	52 39	52 38
100 : 111	8	77 14 —77 38	77 27	—
111 : $\bar{1}$1$\bar{1}$	4	85 14 —85 23	85 19	—

18. 1 : 4-*Bromochlorobenzene-2-sulphanilide.*

This compound crystallises well from acetone in prisms melting at 164°.

System: Monosymmetric.

Axial Ratios: $a : b : c = 1{\cdot}047 : 1 : 1{\cdot}338$; $\beta = 98°30'$.

Equivalence Parameters, taking $2a$ with $W = 68$: $x : y : z = 7{\cdot}776 : 2{\cdot}906 : 3{\cdot}043$.

Forms observed: $\{100\}$, $\{001\}$, $\{101\}$, $\{10\bar{1}\}$, $\{111\}$, $\{11\bar{1}\}$, $\{12\bar{1}\}$.

The following measurements were made:

Angle.	No. of observations.	Limits.	Mean.	Calculated.
$101 : 001$	6	40°57′ — 41°33′	41° 9½′	41°11′
$100 : 101$	8	56 57 — 57 36	57 20	57 19
$100 : \bar{1}01$	9	46 17 — 47 16	46 54	46 45
$10\bar{1} : 00\bar{1}$	7	34 17 — 35 25	34 30	34 45
$100 : 001$	12	98 4 — 98 55	98 29½	98 30
$001 : \bar{1}00$	10	81 6 — 81 50	81 30	81 30
$100 : 111$	25	65 52 — 66 28	66 6	—
$111 : \bar{1}00$	23	113 30 — 114 25	113 52	113 54
$10\bar{1} : 11\bar{1}$	9	37 3 — 37 47	37 24	37 20
$11\bar{1} : 12\bar{1}$	8	18 59 — 19 42	19 20	19 25
$10\bar{1} : 12\bar{1}$	15	56 27 — 56 54	56 45	56 45
$12\bar{1} : \bar{1}21$	25	66 21 — 66 38	66 30	—
$1\bar{1}1 : 111$	31	82 22 — 83 24	82 47	—
$111 : \bar{1}1\bar{1}$	23	96 50 — 97 35	97 14	97 13
$111 : 12\bar{1}$	6	48 52 — 49 22	49 9	49 14

A peculiarity of all the crystals of stable forms of the anilides which we have examined is that most erratic readings are generally obtained from the zone $\{10\bar{1}\}$, $\{11\bar{1}\}$, $\{12\bar{1}\}$, etc., namely, the zone around the prism. After examining a large number of crystals, we found that, as a rule, the form $\{12\bar{1}\}$ is accompanied by another very close to it, the angle between the two varying from 1° to 3°, sometimes one, sometimes the other being absent, however. This explained the erratic readings which had been obtained for the angle $12\bar{1} : \bar{1}21$. On calculating this angle from readings not involving the erratic zone, we found that the smallest readings of the angle—which were remarkably constant—agreed with the calculated value. The same peculiarity was observed in the case of all the anilides of this series that we examined.

3. 1 : 4-*Bromochlorobenzene*-3-*sulphonic Chloride.*

This chloride crystallises with great facility from benzene in rhombs or rhombic plates, melting at 66°. [Found, (sulphonic) Cl = 12·16. Calc., Cl = 12·23 per cent.]

The substance was measured originally by W. T. Gidden. A few measurements which we made agree with his. The axial ratios are calculated from his data.

System: Monosymmetric.

Axial Ratios: $a:b:c=2{\cdot}509:1:1{\cdot}178$; $\beta=97°40'$.

Equivalence Parameters: $x:y:z=5{\cdot}790:2{\cdot}308:2{\cdot}718$.

Angle.	No. of observations.	Mean.	Calculated.
$111 : 1\bar{1}1$	59	96°15′	—
$100 : 111$	81	77 37	—
$100 : 11\bar{1}$	23	68 28	—
$11\bar{1} : \bar{1}1\bar{1}$	24	33 56	33°55′
$110 : 111$	2	39 32	39 34
$111 : \bar{1}\bar{1}1$	7	103 2	103 4
$22\bar{1} : 111$	3	60 55	60 50
$11\bar{1} : 22\bar{1}$	7	16 5	16 6
$22\bar{1} : 110$	3	21 19	21 16

4. 1 : 4-*Chlorobromobenzene-2-sulphonic Bromide.*

This bromide was measured by Gidden. It crystallises readily from benzene in the usual rhombs (m. p. 110°) characteristic of these compounds.

System: Monosymmetric.

Axial Ratios, calculated from Gidden's data: $a:b:c=2{\cdot}531:1:1{\cdot}171$; $\beta=98°35'$.

Equivalence Parameters: $x:y:z=5{\cdot}840:2{\cdot}307:2{\cdot}702$.

Angle.	No. of observations.	Mean.	Calculated.
$111 : 1\bar{1}1$	40	96°17′	—
$100 : 111$	38	78 22	—
$110 : \bar{1}1\bar{1}$	6	51 55	—
$110 : 111$	2	39 56	39°58′
$111 : 001$	8	53 13	53 12
$100 : 00\bar{1}$	2	81 3	81 25
$100 : 110$	4	68 10	68 13

17. 1 : 4-*Chlorobromobenzene-2-sulphanilide.*

This affords an example of a dimorphous substance. When pure it crystallises from acetone in a labile form. When the bright crystals are removed from the solution in which they have been formed, they rapidly become opaque and the crystal faces become covered with a fine powder. These crystals are very soft and fall to powder under slight pressure. Owing to the rapidity with which transition from the labile to the stable form takes place, great difficulty is experienced in obtaining measurements of these crystals. A few angles were determined, however, which proved that the crystals are isomorphous with the labile form of *p*-dibromobenzenesulphanilide, which we were able to measure completely. The habit and forms present also prove this to be the case.

If a small quantity of aniline be present in the acetone solution, the sulphanilide crystallises in a stable form isomorphous with

2-bromo-5-chlorobenzenesulphanilide; thus the labile or stable form can be obtained at will. At times both forms have developed simultaneously in the same solution; this has also been observed to take place in the case of *p*-dibromobenzenesulphanilide. Both forms melt at 138°.

(Stable form).—System: Monosymmetric.
Axial Ratios: $a : b : c = 1{\cdot}058 : 1 : 1{\cdot}3395$; $\beta = 98°7'$.
Equivalence Parameters: $x : y : z = 7{\cdot}752 : 2{\cdot}894 : 3{\cdot}062$. [2*a*.]
Forms present: {001}, {101}, {$\bar{1}01$}, {111}, {$11\bar{1}$}, {$12\bar{1}$}.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
101 : 001	10	56°32′—57° 8′	56°47′	56°46′
001 : $\bar{1}01$	11	46 38 —46 56	46 45	—
$\bar{1}01$: $\bar{1}0\bar{1}$	11	76 9 —76 50	76 29	—
111 : 101	16	41 14 —41 53	41 28	41 30½
111 : $1\bar{1}1$	15	82 46 —83 25	83 1	—
111 : $\bar{1}1\bar{1}$	5	96 40 —97 8	96 57	96 59
111 : $11\bar{1}$	6	56 39 —57 37	56 56	57 6
$11\bar{1}$: $00\bar{1}$	5	56 43 —57 40	57 7	57 8
001 : 111	16	65 33 —66 9	65 48	65 46

23. 1 : 4-*Chlorobromobenzene-2-sulpho-o-toluidide.*

This compound crystallises extremely well from acetone; it melts partly at 143—144°, then resolidifies above that temperature and melts sharply at 151°. When suddenly cooled, it assumes the vitreous form; when gently warmed, this crystallises in the form which has the lower melting point, the substance melting completely at 143—144° and not resolidifying. It is evident from this that the form stable at the ordinary temperature is that melting at 143°, which is metastable at its melting point.

System: Monosymmetric.
Axial Ratios: $a : b : c = 0{\cdot}727 : 1 : 1{\cdot}195$; $\beta = 102°5'$.
Equivalence Parameters: $x : y : z = 8{\cdot}122 : 2{\cdot}792 : 3{\cdot}262$. [4*a*.]
Forms observed: {001}, {010}, {101}, {101}, {011}.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
001 : 101	12	67°30′— 68° 8′	67°47′	—
101 : $10\bar{1}$	10	61 49 — 62 21	62 7	—
$10\bar{1}$: $00\bar{1}$	11	49 20 — 50 35	50 4	50 6′
001 : 011	26	49 10 — 49 38	49 27	—
011 : 010	7	40 21 — 40 48	40 31	40 33
001 : 010	10	89 45 — 90 15	90 0	90 0
101 : 011	15	75 28 — 76 5	75 44	75 46
011 : $\bar{1}01$	16	103 50 —104 39	104 17	104 14
$\bar{1}01$: 011	12	65 8 — 65 30	65 20	65 21
011 : 101	12	114 20 —114 52	114 41	114 39

24. 1 : 4-*Chlorobromobenzene*-2-*sulpho*-m-*toluidide.*

This compound crystallises readily from acetone in six-sided rhombs (m. p. 159·5°) the edges and corners of which are truncated. The four faces of the form {011} were useless for measurement, as they gave multiple reflexions in every case.

System: Monosymmetric.
Axial Ratios: $a : b : c = 0{\cdot}7576 : 1 : 1{\cdot}154$; $\beta = 100°37'$.
Equivalence Parameters: $x : y : z = 8{\cdot}430 : 2{\cdot}782 : 3{\cdot}210$. [4*a*.]
Forms observed: {011}, {$10\bar{1}$}, {110}, {101}, {001}.

Angle.	No of observations.	Limits.	Mean.	Calculated.
001 : 101	20	49° 0′— 49°58′	49°27′	49°28′
101 : $10\bar{1}$	47	65 52 — 66 31	66 12	—
$10\bar{1}$: $00\bar{1}$	22	63 49 — 64 46	64 21	64 21
101 : 110	27	45 41 — 46 17	45 58	—
110 : $01\bar{1}$	7	69 20 — 69 40	69 30	69 30
$01\bar{1}$: $\bar{1}0\bar{1}$	19	64 70 — 64 50	64 26	64 32
$\bar{1}01$: 011	40	72 51 — 73 59	73 19	73 21
011 : 110	16	56 25 — 57 23	56 50	56 56
110 : $10\bar{1}$	28	49 12 — 50 13	49 43	—
110 : $1\bar{1}0$	6	73 7 — 73 42	73 21	73 21
110 : $\bar{1}10$	6	106 25 —106 57	106 36	106 39

25. 1 : 4-*Chlorobromobenzene*-2-*sulpho*-p-*toluidide.*

This toluidide crystallises readily from acetone in prisms (m. p. 157°) remarkable on account of the number of faces that in most cases are developed upon them. They show a decided resemblance in habit and dimensions to the stable form of the anilide.

System: Monosymmetric.
Axial Ratios: $a : b : c = 0{\cdot}767 : 1 : 0{\cdot}959$; $\beta = 98°25'$.
Equivalence Parameters: $9{\cdot}022 : 2{\cdot}940 : 2{\cdot}820$. [4*a*.]
Forms observed: {100}, {010}, {001}, {011}, {012}, {212}, {$12\bar{1}$}, {$11\bar{1}$}, {101}, {$\bar{1}01$}.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100 : 101	4	41°39′—42° 9′	41°56′	41°52′
101 : 001	11	56 14 —56 53	56 33	—
100 : 001	5	98 16 —98 41	98 30	98 25
$\bar{1}\bar{1}1$: $\bar{1}11$	31	57 24 —58 42	58 3	58 1
$\bar{1}11$: $\bar{1}21$	24	18 8 —19 57	18 55	18 57
011 : 012	23	25 1 —25 45	25 23	25 23
012 : 011	21	17 30 —18 36	18 5	18 7
101 : 212	10	17 10 —18 13	17 48	17 45
212 : 010	2	72 11 —72 15	72 13	72 15
101 : 012	10	59 47 —60 18	60 7	60 8
$\bar{1}0\bar{1}$: $\bar{1}11$	13	78 30 —79 26	78 49	—
$\bar{1}11$: 012	20	40 38 —41 28	41 31	—
111 : 011	5	39 18 —39 59	39 31	39 26

7. 1 : 4-*Dibromobenzenesulphonic Chloride.*

p-*Dibromobenzenesulphonic chloride* crystallises readily in measurable form from a mixture of benzene and light petroleum; it melts at 71°. (Found, Cl = 10·79. Calc., Cl = 10·61 per cent.)

System: Monosymmetric.
Axial Ratios: $a : b : c = 2{\cdot}476 : 1 : 1{\cdot}1439$; $\beta = 95°26'$.
Equivalence Parameters: $x : y : z = 5{\cdot}787 : 2{\cdot}337 : 2{\cdot}674$.
Forms observed: $\{100\}$, $\{111\}$, $\{\bar{1}11\}$, $\{100\}$, $\{22\bar{1}\}$.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
$100 : 111$	19	76° 2′—76°41′	76°22′	—
$111 : \bar{1}11$	4	33 38 —34 30	34 1	33°51′
$\bar{1}11 : \bar{1}00$	4	69 41 —69 53	69 44	69 47
$111 : \bar{1}1\bar{1}$	11	85 39 —86 28	85 57	—
$100 : 110$	13	67 32 —68 15	67 55	—
$110 : \bar{1}10$	7	43 33 —44 30	44 5	44 10
$111 : 110$	5	39 16 —40 42	39 51	39 55
$110 : 11\bar{1}$	5	38 11 —39 31	38 37	38 28

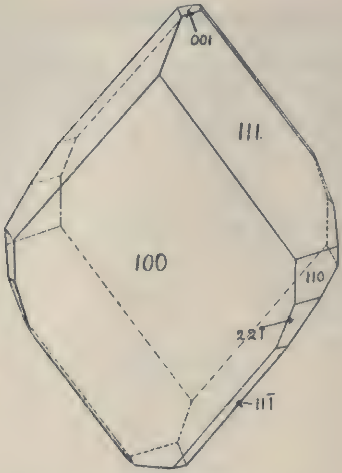
8. 1 : 4-*Dibromobenzenesulphonic Bromide.*

p-*Dibromobenzenesulphonic bromide* crystallises well from a mixture of benzene and light petroleum in forms closely resembling the sulphonic chloride. It melts at 114°. [Found, (sulphonic) Br = 20·96. Calc., Br = 21·10 per cent.]

System: Monosymmetric.
Axial Ratios: $a : b : c = 2{\cdot}479 : 1 : 1{\cdot}445$; $\beta = 96°49'$.
Equivalence Parameters: $x : y : z = 5{\cdot}796 : 2{\cdot}338 : 2{\cdot}676$.
Forms present: $\{100\}$, $\{111\}$, $\{\bar{1}11\}$, $\{110\}$, $\{22\bar{1}\}$, $\{001\}$.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
$100 : 111$	27	77° 0′—77°29′	77°12′	—
$111 : \bar{1}11$	6	33 41 —34 7	33 48	33°51′
$\bar{1}11 : \bar{1}00$	6	68 32 —68 49	68 41	68 57
$111 : \bar{1}1\bar{1}$	13	85 15 —85 40	85 29	—
$100 : 110$	18	67 25 —68 21	67 53	—
$110 : \bar{1}10$	7	44 3 —44 27	44 14	44 14
$00\bar{1} : 11\bar{1}$	4	49 13 —49 18	49 15	49 18
$11\bar{1} : 22\bar{1}$	6	16 8 —16 27	16 18	16 22
$22\bar{1} : 110$	7	21 34 —22 2	21 45	21 48
$110 : 111$	11	39 53 —40 25	40 6	40 13
$111 : 001$	4	52 5 —52 27	52 18	52 19
$100 : 00\bar{1}$	8	82 40 —83 40	83 6	83 11
$111 : \bar{1}10$	7	53 2 —53 42	53 18	53 21
$11\bar{1} : 111$	[illegible]	78 4 —78 41	78 22	78 23

FIG. 1.



p-*Dibromobenzenesulphonic bromide.*

19. 1:4-*Dibromobenzenesulphanilide.*

p-*Dibromobenzenesulphanilide.*—This substance was obtained in two forms, a labile and a stable form, under conditions exactly similar to those which gave rise to two forms of the chlorobromo-compound. In this case both forms were measured.

The *labile* form crystallises well from a solution of the pure substance in acetone; it melts at 143°.

System: Monosymmetric.

Axial Ratios: $a:b:c = 1{\cdot}392:1:1{\cdot}163$; $\beta = 97°50'$.

Equivalence Parameters: $x:y:z = 7{\cdot}631:2{\cdot}781:3{\cdot}210$. [2*a*.]

Forms present: $\{100\}$, $\{010\}$, $\{111\}$, $\{\bar{1}11\}$, $\{121\}$.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
010 : 111	11	46°27′—46°51′	46°37′	—
010 : 121	8	27 33 —28 2	27 44	27°54′
121 : 111	8	18 38 —18 58	18 49	18 44
010 : $\bar{1}$11	20	50 2 —50 57	50 29	—
100 : 111	11	57 47 —58 41	58 7	58 12
111 : $\bar{1}$11	11	69 26 —70 15	69 51	—
$\bar{1}$11 : $\bar{1}$00	9	51 33 —52 18	51 59	51 57
100 : 010	4	89 43 —90 16	89 59	90 0

The *stable* form separates in measurable crystals from a solution of the substance in acetone containing a trace of aniline. It melts at 143°.

System: Monosymmetric.

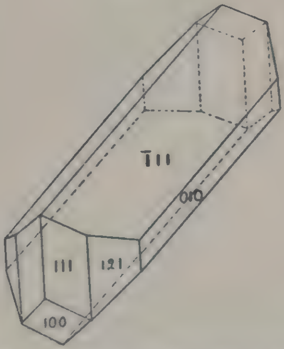
Axial Ratios: $a:b:c = 1{\cdot}329:1:1{\cdot}025$; $\beta = 97°58'$.

Equivalence Parameters: $x:y:z = 7{\cdot}793:2{\cdot}932:3{\cdot}005$. [2*a*.]

Forms present: $\{001\}$, $\{101\}$, $\{\bar{1}01\}$, $\{111\}$, $\{11\bar{1}\}$, $\{12\bar{1}\}$.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
10$\bar{1}$: 101	11	74°47′ — 75°28′	75° 7′	—
101 : 001	14	57 12 — 57 44	57 26	57°26′
001 : $\bar{1}$01	12	47 20 — 47 33	47 26	47 27
001 : 111	14	65 47 — 66 10	65 58	—
111 : 11$\bar{1}$	8	56 24 — 57 16	56 38	56 42
11$\bar{1}$: 00$\bar{1}$	6	56 58 — 57 53	57 23	57 20
111 : 00$\bar{1}$	15	113 49 —114 18	114 0	114 2
$\bar{1}$1$\bar{1}$: 111	8	98 0 — 98 35	98 22	98 22
111 : 101	19	40 24 — 41 7	40 48	40 49
111 : 1$\bar{1}$1	16	81 20 — 82 0	81 38	—
10$\bar{1}$: 11$\bar{1}$	22	36 24 — 37 42	37 5	37 3
11$\bar{1}$: 12$\bar{1}$	8	18 58 — 19 51	19 22	19 25
12$\bar{1}$: $\bar{1}$21	7	67 2 — 67 8	67 6	67 4
111 : 12$\bar{1}$	9	49 1 — 49 34	49 17	49 17
12$\bar{1}$: $\bar{1}$1$\bar{1}$	9	130 24 —131 2	130 42	130 43

FIG. 2.



Labile form of p-*dibromobenzenesulphanilide.*

26. 1 : 4-*Dibromobenzenesulpho*-p-*toluidide.*

p-*Dibromobenzenesulpho*-p-*toluidide* separates readily in measurable forms from acetone. It melts at 151°.

System : Monosymmetric.

Axial Ratios : $a : b : c = 0{\cdot}7645 : 1 : 0{\cdot}9595$; $\beta = 98°32'$.

Equivalence Parameters : $x : y : z = 9{\cdot}001 : 2{\cdot}943 : 2{\cdot}824$. [4*a.*]

Forms present : {010}, {100}, {001}, {101}, {$\bar{1}$01}, {011}, {012}, {111}, {111}, {212}.

Angle.	No. of observations.	Limits.	Mean.	Calculated
$\bar{1}$11 : 010	42	60°32′—61°30′	61° 2′	—
011 : 010	26	46 5 —47 12	46 28	—
011 : $\bar{1}$11	28	39 0 —39 51	39 30	—
$\bar{1}$11 : 1$\bar{1}$1	37	57 0 —58 37	58 0	57°56′
001 : 012	19	25 10 —25 55	25 28	25 25
012 : 011	24	17 24 —18 40	17 57	18 7
001 : 010	9	89 41 —90 11	89 59	90 0
100 : 111	3	50 57 —51 6	51 1	51 5
111 : 011	5	45 3 —45 18	45 13	45 6
$\bar{1}$11 : $\bar{1}$00	6	44 2 —44 38	44 17	44 19
101 : 211	6	17 14 —18 9	17 44	17 44
212 : 111	5	14 37 —15 5	14 47	14 52
111 : 010	3	57 21 —57 41	57 29	57 24

27. *Methylic* p-*Dibromobenzenesulphonate.*

This crystallises readily from acetone. It melts at 63°.

System: Monosymmetric.
Axial Ratios: $a:b:c = 1{\cdot}167:1:2{\cdot}443$; $\beta = 94°0'$.
Equivalence Parameters: $x:y:z = 2{\cdot}930:2{\cdot}454:5{\cdot}995$.
Forms present: {100}, {101}, {$\bar{1}01$}, {111}, {210}.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100 : 210	23	49°59′— 51°26′	50°37′	—
210 : $\bar{2}10$	9	78 17 — 79 17	78 39	78°46′
100 : 111	15	74 37 — 75 38	75 5	—
111 : $\bar{1}00$	15	104 36 —105 27	104 57	104 55
101 : 111	10	46 26 — 47 54	47 13	—
111 : $\bar{1}1\bar{1}$	6	85 3 — 85 42	85 32	85 34
100 : 101	5	67 9 — 68 18	67 57	67 44
101 : $\bar{1}01$	6	50 19 — 51 38	51 2	51 3
$\bar{1}01$: $\bar{1}00$	12	60 25 — 61 20	60 52	61 13
$\bar{1}01$: 111	4	64 3 — 65 4	64 41	64 43
111 : 210	6	42 50 — 43 29	43 7	43 4
210 : $10\bar{1}$	5	71 34 — 72 53	72 16	72 13

28. *Ethylic* p-*dibromobenzenesulphonate.*

This separates fairly readily from acetone but the forms appearing are so few that very few angles have been measured. It melts at 106°.

System: Orthorhombic.
Axial Ratios: $a:b:c = 1{\cdot}124:1:0{\cdot}9393$.
Equivalence Parameters: $x:y:z = 6{\cdot}455:2{\cdot}872:2{\cdot}697$. [2*a*.]
Forms observed: {100}, {101}, {110}, {010}.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
010 : 110	11	41° 8′—42° 4′	41°41′	—
010 : 011	34	46 29 —47 21	46 49	—

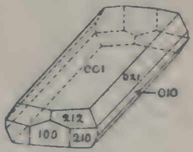
9. 1 : 4-*Iodochlorobenzene-2-sulphonic Chloride.*

p-*Iodochlorobenzenesulphonic chloride* is readily obtained in good prismatic crystals (m. p. 69°) from a mixture of benzene and light petroleum. [Found, (sulphonic) Cl = 10·53. Calc., Cl = 10·52 per cent.]

System: Monosymmetric.
Axial Ratios: $a:b:c = 0{\cdot}729:1:0{\cdot}654$; $\beta = 99°42'$.
Equivalence Parameters: $x:y:z = 3{\cdot}095:4{\cdot}247:2{\cdot}778$.
Forms present: {010}, {001}, {021}, {100}, {210}, {221}.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100 : 210	9	17°39′—18°11′	17°51′	17°52′
210 : 010	12	71 43 —72 27	72 8	—
010 : 021	15	34 31 —35 30	34 49	34 50
021 : 001	11	54 54 —55 32	55 10	—
100 : 001	3	99 39 —99 43	99 41	99 42
001 : 210	8	98 50 —99 27	99 13	—
001 : 212	10	54 33 —55 25	54 54	54 53
212 : 210	6	43 55 —44 35	44 12	44 20
010 : 212	12	75 6 —75 28	75 18	75 16
212 : $2\bar{1}2$	3	29 20 —29 31	29 24	29 28
100 : 010	[illegible]	89 50 —90 17	90 1	90 0
010 : 001	12	89 47 —90 12	89 59	90 0

FIG. 3.



5-Chloro-2-iodobenzenesulphonic chloride.

9. 1 : 4-*Iodochlorobenzene-2-sulphonic Bromide.*

p-*Iodochlorobenzenesulphonic bromide* crystallises readily from a mixture of benzene and light petroleum in four-sided prisms with pyramidal ends. Although differing entirely from *p*-dibromobenzenesulphonic bromide in habit, when the correct faces are chosen as pinacoids the axial ratios deduced for this bromide are almost identical with those of that substance. It melts at 102°. [Found Br = 21·30. Calc., Br = 20·98 per cent.]

System : Monosymmetric.

Axial Ratios : $a : b : c = 2·469 : 1 : 1·154$; $\beta = 95°50'$.

Equivalence Parameters : $x : y : z = 5·761 : 2·333 : 2·692$.

Forms present : {100}, {101}, {111}, {210}.

Angle.	No of observations.	Limits.	Mean.	Calculated.
100 : 210	33	50°30′—51° 9′	50°51′	—
210 : $\bar{2}10$	14	78 8 —78 29	78 19	78 18′
101 : 111	10	47 6 —47 32	47 17	—
111 : $\bar{1}1\bar{1}$	5	85 13 —85 34	85 25	85 26
100 : 101	12	69 29 —70 12	69 48	—
210 : $\bar{1}11$	4	43 59 —44 11	44 5	44 9
100 : 111	2	76 14 —76 21	76 18	76 27
101 : 210	10	77 6 —77 37	77 24	77 26
210 : 111	3	65 1 —65 13	65 5	65 3

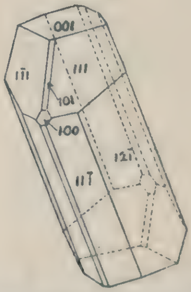
20. 1 : 4-*Iodochlorobenzene-2-sulphanilide.*

This separates readily from acetone in a form closely resembling the stable forms of the anilides previously measured. It melts at 168°.

System: Monosymmetric.
Axial Ratios: $a:b:c = 1{\cdot}350:1:0{\cdot}9971$; $\beta = 97°15'$.
Equivalence Parameters: $x:y:z = 7{\cdot}943:2{\cdot}942:2{\cdot}933$. [2*a*.]
Forms present: $\{100\}, \{001\}, \{10\bar{1}\}, \{101\}, \{11\bar{1}\}, \{111\}, \{12\bar{1}\}$.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
$10\bar{1} : 100$	7	33°35′—33°55′	33°49′	33°50′
$100 : 101$	4	38 51 —39 4	38 58	38 56
$101 : 001$	6	58 4 —58 25	58 14	58 19
$100 : 001$	13	97 1 —97 29	97 15	—
$001 : \bar{1}01$	9	48 32 —49 7	48 50	48 55
$001 : 111$	23	66 5 —66 49	66 23	—
$111 : 11\bar{1}$	21	55 2 —55 42	55 22	55 19
$11\bar{1} : 00\bar{1}$	22	57 57 —58 34	58 15	58 18
$\bar{1}1\bar{1} : 111$	9	99 14 —99 37	99 24	99 24
$111 : 101$	7	40 13 —40 23	40 16	40 18
$111 : 1\bar{1}1$	11	80 23 —80 56	80 36	80 36
$10\bar{1} : 11\bar{1}$	7	36 46 —37 31	36 56	36 56
$11\bar{1} : 12\bar{1}$	20	19 0 —19 52	19 21	19 26
$12\bar{1} : \bar{1}21$	13	67 15 —67 31	67 23	67 16
$100 : 111$	19	53 26 —53 48	53 37	—
$111 : \bar{1}11$	20	77 39 —78 18	77 57	77 59
$\bar{1}11 : \bar{1}00$	19	48 7 —48 44	48 25	48 24
$111 : 12\bar{1}$	7	48 4 —48 46	48 25	48 25
$111 : \bar{1}21$	4	65 29 —65 45	65 35	65 35

FIG. 4.



5-Chloro-2-iodobenzenesulphanilide.

29. *Ethylic* 1 : 4-*Iodochlorobenzene-2-sulphonate.*

This separates from ether in thin, hexagonal plates melting at 87°.

System: Orthorhombic.
Axial Ratios: $a:b:c = 2{\cdot}322:1:0{\cdot}898$.
Equivalence Parameters: $x:y:z = 6{\cdot}697:2{\cdot}883:2{\cdot}589$. [2*a*.]
Forms present: $\{001\}, \{100\}, \{110\}, \{111\}, \{201\}$.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100 : 110	21	66°10′—67°10′	66°42′	—
110 : 010	8	23 3 —23 34	23 13	23°18′
110 : $\bar{1}10$	7	46 9 —47 6	46 35	46 36
100 : 010	10	89 47 —90 20	89 59	90 0
100 : 111	17	73 22 —74 27	73 57	—
111 : $\bar{1}11$	6	31 51 —32 13	32 4	32 6
100 : 201	12	51 45 —52 53	52 9	52 18

14. 1 : 4-*Iodobromobenzene-2-sulphonic Chloride.*

From benzene and light petroleum this separates in forms that are very similar indeed to those of the corresponding chloroiodo-compound. It melts at 97°. (Found, Cl = 9·32. Calc., Cl = 9·30 per cent.)

System : Monosymmetric.
Axial Ratios : $a:b:c = 0·815:1:0·673$; $\beta = 95°28'$.
Equivalence Parameters : $x:y:z = 3·291:4·040:2·719$.
Forms present : {010}, {001}, {021}, {212}, {211}.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
001 : 021	21	58°11′— 58°35′	58°20′	—
021 : 010	17	31 17 — 31 54	31 39	31°40′
001 : 010	20	89 45 — 90 15	90 0	90 0
001 : 212	23	54 53 — 55 20	55 9	—
212 : $00\bar{1}$	20	124 40 —124 58	124 50	124 51
010 : 212	19	74 37 — 75 8	74 48	—
212 : $2\bar{1}2$	13	30 7 — 30 41	30 21	30 24
021 : 212	4	58 26 — 58 33	58 29	58 28
212 : 211	3	17 59 — 18 10	18 4	18 1

21. 1 : 4-*Iodobromobenzene-2-sulphanilide.*

This anilide separates readily from acetone. It melts at 150°.

System : Monosymmetric,
Axial Ratios : $a:b:c = 1·329:1:0·979$; $\beta = 97°18'$.
Equivalence Parameters : $x:y:z = 7·909:2·976:2·913$. [2*a*.]
Forms present : {100}, {001}, {101}, {101}, {111}, {111}, {121}.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100 : 001	3	97° 4′— 97°10′	97° 7′	97°18′
100 : 101	3	38 41 — 39 20	38 54	38 53
101 : 001	3	58 9 — 58 29	58 20	58 25
001 : $\bar{1}01$	5	48 47 — 49 16	49 1	48 57
$\bar{1}01$: $\bar{1}00$	1	33°44′	33 44	33 45
111 : 111	20	79 14 — 80 5	79 40	—
111 : $\bar{1}1\bar{1}$	20	99 56 —100 48	100 19	100 20
$10\bar{1}$: $11\bar{1}$	7	36 15 — 36 55	36 38	36 27
111 : 121	6	18 55 — 19 23	19 7	19 27
121 : $\bar{1}21$	15	68 3 — 68 27	68 12	—
001 : 111	35	65 40 — 66 48	66 17	—
111 : 111	17	55 11 — 56 8	55 28	55 36
111 : 001	19	57 49 — 58 35	58 22	58 7

As is generally the case, the face $\{11\bar{1}\}$ is very bad indeed, accounting for the discrepancy between the mean observed and calculated values of the angles over this face.

10. 1 : 4-*Chloriodobenzene-2-sulphonic Chloride.*

This crystallises readily from a mixture of benzene and light petroleum. It melts at 88°. [Found, (sulphonic) Cl = 10·50. Calc., Cl = 10·52 per cent.]

System : Monosymmetric.
Axial Ratios : $a : b : c = 2·583 : 1 : 1·176$; $\beta = 99°7'$.
Equivalence Parameters : $x : y : z = 5·914 : 2·289 : 2·692$.
Forms present : $\{100\}$, $\{110\}$, $\{111\}$, $\{\bar{1}11\}$, $\{22\bar{1}\}$.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
$100 : 111$	43	78°47′— 79°21′	79° 0′	—
$111 : \bar{1}11$	14	32 42 — 33 14	32 59	32°57′
$\bar{1}11 : \bar{1}00$	14	67 49 — 68 17	68 3	—
$111 : \bar{1}1\bar{1}$	18	82 58 — 83 30	83 13	—
$\bar{1}1\bar{1} : \bar{1}\bar{1}\bar{1}$	20	96 35 — 97 8	96 47	96 47
$11\bar{1} : 22\bar{1}$	6	15 58 — 16 10	16 3	16 3
$22\bar{1} : 110$	7	21 12 — 21 33	21 21	21 22
$110 : 111$	8	39 42 — 40 14	39 58	40 1
$111 : \bar{1}\bar{1}1$	7	102 20 —102 46	102 34	102 34
$100 : 110$	8	68 16 — 68 38	68 25	68 35

12. 1 : 4-*Bromoiodobenzene-2-sulphonic Chloride.*

This crystallises in a labile form from a mixture of benzene and light petroleum. It melts at 91°. (Found, Cl = 9·32. Calc., Cl = 9·30 per cent.)

System : Monosymmetric.
Axial Ratios : $a : b : c = 2·555 : 1 : 1·158$; $\beta = 94°23'$.
Equivalence Parameters : $x : y : z = 5·882 : 2·302 : 2·666$.
Forms present : $\{100\}$, $\{110\}$, $\{111\}$, $\{\bar{1}11\}$.

Angle.	No of observations.	Limits.	Mean.	Calculated.
$100 : 111$	10	75°40′— 76°21′	76° 8′	—
$111 : \bar{1}11$	10	32 51 — 33 7	33 1	—
$\bar{1}11 : \bar{1}00$	8	70 29 — 71 29	70 51	70°51′
$111 : \bar{1}1\bar{1}$	4	94 27 — 94 44	94 35	—
$100 : 110$	10	68 32 — 68 54	68 40	68 34
$111 : \bar{1}\bar{1}1$	5	102 3 —102 28	102 13	102 12
$\bar{1}\bar{1}1 : \bar{1}\bar{1}0$	3	38 13 — 38 23	38 18	38 18

22. 1 : 4-*Chloriodobenzene-2-sulphonic Bromide.*

This crystallises readily from benzene. It melts at 143°. (Found, Br = 21·10. Calc., Br = 20·98 per cent.)

System : Monosymmetric.
Axial Ratios : $a : b : c = 2·567 : 1 : 1·167$; $\beta = 100°30'$.
Equivalence Parameters : $x : y : z = 5·912 : 2·303 : 2·689$.
Forms present : $\{100\}$, $\{001\}$, $\{110\}$, $\{11\bar{1}\}$, $\{111\}$, $\{22\bar{1}\}$.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100 : 111	17	79°36′— 79°55′	79°47′	—
$111 : \bar{1}00$	19	100 1 —100 30	100 14	100°13′
100 : 110	14	68 12 — 68 33	68 23	—
$110 : \bar{1}10$	6	43 8 — 43 27	43 14	43 14
$1\bar{1}1 : 111$	10	96 23 — 97 26	96 44	96 44
$111 : \bar{1}1\bar{1}$	10	82 45 — 83 39	83 17	83 16
100 : 001	5	100 9 —100 45	100 29	100 30
$001 : \bar{1}00$	5	79 10 — 79 47	79 30	79 30
001 : 111	7	53 5 — 53 38	53 22	53 20
111 : 110	11	40 17 — 40 45	40 31	—
$110 : 22\bar{1}$	17	21 15 — 21 40	21 23	21 28
$22\bar{1} : 00\bar{1}$	3	64 28 — 64 53	64 45	64 41
$100 : 22\bar{1}$	8	66 8 — 66 34	66 20	66 24

16. 1 : 4-*Dichlorobenzene-2-sulphonamide.*

This substance crystallises from a mixture of acetone and ethylic acetate in bright plates, which are very much given to twinning. It melts at 182°.

System : Monosymmetric ; $a : b : c = 0{\cdot}423 : 1 : 0{\cdot}421$; $\beta = 91°44'$.

Equivalence Parameters : 2·573 : 6·079 : 2·558.

Forms present : {010}, {110}, {021}, {111}, $\{\bar{1}11\}$.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
010 : 110	19	66°52′—67°16′	67° 4′	—
$110 : 1\bar{1}0$	8	45 36 —46 4	45 50	45°52′
010 : 021	17	49 37 —50 18	49 56	—
$\bar{1}10 : 021$	10	76 26 —76 56	76 43	76 44
021 : 111	4	44 37 —44 55	44 44	44 47
$111 : 1\bar{1}0$	4	58 21 —58 51	58 32	58 29
021 : 110	15	73 51 —74 34	74 13	—
$110 : 1\bar{1}\bar{1}$	4	59 46 —60 3	59 53	60 4
$1\bar{1}\bar{1} : 0\bar{2}\bar{1}$	5	45 21 —46 1	45 41	45 43
010 : 111	6	73 34 —73 44	73 40	73 37

The substance exhibits pseudo-cubic symmetry, the parameters *a* and *c* being practically equal. This is evidence of the existence in the structure of the rhombohedral type of marshalling.

CXLIX.—*The Molecular Complexity of Amides in Various Solvents. Part II.*

By Andrew Norman Meldrum (Carnegie Research Fellow) and William Ernest Stephen Turner.

Two years ago the authors communicated the results of a study of the molecular complexity of eleven amides (simple and substituted) in each of the solvents, water, alcohol, acetone, chloroform, ether, and benzene (Trans., 1908, **93**, 876). These solvents were suitable for our purpose by reason of their dielectric constants, which range, at ordinary temperatures, from about 80 in the case of water to 2 for benzene. Our principal object was to test the soundness of what may be called the Nernst-Thomson rule, that the tendency of the solute to molecular association is hindered or allowed according as the dielectric constant of the solvent is high or low. We were successful to a considerable degree in demonstrating that the rule is sound. Special attention should be drawn to our results in the case of ether, which had been regarded as preventing association of the solute (Beckmann, *Zeitsch. physikal. Chem.*, 1890, **6**, 455). We found that this solvent is an associating one, as by reason of its low dielectric constant it ought to be. In the case of water, however, we found important exceptions to the rule. We desired to confirm and extend these observations, particularly as regards ether and water. Other points of interest arose: for example, we wished to observe the alteration in the degree of association in the passage from member to member of a series of aliphatic amides.

In the investigation which we now describe, we examined seventeen additional substances of the amide type, including carbamides, anilides, and urethanes, using the same organic solvents as before. The data regarding amides in aqueous solution, which present some remarkable features, are reserved for another communication. The particular boiling-point process by which the molecular weights were determined has been subjected by one of us to a thorough scrutiny (Turner, this vol., p. 1184).

In our earlier paper we pointed out that the two methods of determining the amount of the solvent, by weighing, and by reading the volume of the solution—the method adopted by Lumsden and Walker—lead to results which differ little unless the solution is a concentrated one. We therefore adopted the volume method, with the proviso that we should make a special comparison of the extent of association of different substances only in dilute solution.

At the outset of the second part of our work, especially in view of the advance in accuracy obtained by using the new form of apparatus, we had to consider again how the amount of solvent should be determined.

It may be remarked that the difference between the two sets of molecular-weight data is to be ascribed chiefly to the inclusion, in the volume of the solution, of the solution-volume of the solute itself. The difference therefore should be least in those solutions in which contraction occurs when solvent and solute are mixed.

An endeavour has been made, when the solubility of the amides would allow of it, to determine the molecular weights of the various substances in solutions of approximately equimolecular concentration. As a consequence, the quantity of substance required is greater the higher its molecular weight. At the same time, the greater proportion of the volume of the solution occupied by the solute results in a greater difference between the two sets of data (the weight and volume sets). On the whole, however, the actual percentage difference between the two sets, at the standard concentration adopted of 30 milligram-molecules per 100 c.c., is nearly the same, amounting to about 3 per cent.

In view of the smallness of the differences at the standard concentration, it appeared to us advantageous to adhere to the volume-method, and thus to put ourselves in the position of being able to compare our present with our previous results. In order to illustrate the nature of the differences between the two methods, we have quoted both weight and volume results, for solutions in alcohol, acetone, benzene, and chloroform, of propionamide, as a typical aliphatic amide, and methylacetanilide, as containing the phenyl group. In the case of all other amides, in those solvents and in ether as well, we have given only the volume data.

EXPERIMENTAL.

Most of the materials were obtained from Kahlbaum, and were crystallised until of constant melting point. The determination of this was carried out by means of a melting-point flask with long neck, and a series of standardised short-stem thermometers. The numbers enclosed in parentheses are those quoted by Beilstein: Propionamide 80° (79°), valeramide 126·5° (127°), *n*-butyramide 114—114·4° (115°), *iso*butyramide 127·5° (128—129°), *iso*butylacetamide 118—118·8° (120°), were crystallised from benzene; phenylcarbamide 146·5—147° (147°), diphenylcarbamide 239—240° (235°), phenylacetamide 157° (154—155°), urethane 49° (49—50°), from alcohol; ethylacetanilide 53° (54·5°), and methylacetanilide, of which the original specimen and all crops melted at 98—99° (101—102°), from ether; and lactanilide 58·5—59·1° (58°) from water. Formanilide, in the purification of which considerable difficulty was at first encountered, was finally found to yield beautiful, colourless, needle-shaped crystals when excess of the substance was boiled with light petroleum (b. p. 60—80°) and the excess allowed to solidify under the solvent, m. p. 47—47·5° (46°). The solvents were carefully purified and fractionally distilled as described in our previous communication. The constants used were as follows:

	Volume.	Weight.
Alcohol	1590	1170
Acetone	2270	1720
Chloroform ...	2770	3900
Ether	3100	2160
Benzene	3200	2610

One change has been made in the constants used in the previous communication, namely, in that for chloroform (compare Beckmann, *Zeitsch. physikal. Chem.*, 1908, **63**, 177; and Turner, this vol., p. 1192). The older results in chloroform solution, wherever they are quoted in this paper, have been recalculated on the new basis.

In the tables which follow:

N_v denotes the number of milligram-molecules per 100 c.c. of solution.
N_w ,, ,, ,, ,, 100 g. ,,
M.W.$_v$,, molecular weight determined by the volume method.
M.W.$_w$,, ,, ,, ,, weight ,,

Solvent—Alcohol.

V.	*W.*	Δ.	N_v.	M.W.$_v$.	M.W.$_w$.
		Propionamide (M.W. 73·1), 1·549 grams.			
26·3	18·62	1·178	80·7	79·6	82·6
32·4	23·36	0·944	65·4	80·6	82·2
37·8	27·54	0·803	56·0	81·1	82·0
44·3	31·90	0·694	47·8	80·1	81·9
50·0	36·38	0·610	42·4	80·7	81·7
		Methylacetanilide (M.W. 149), 2·880 grams.			
24·7	16·41	1·369	78·2	135	150
32·5	21·88	1·039	59·4	136	148·5
41·5	28·64	0·804	46·5	137	146
51·4	35·77	0·642	37·6	139	147
60·7	42·65	0·542	31·8	139	146

V.	Δ.	N_v.	M.W.$_v$.	*V.*	Δ.	N_v.	M.W.$_v$.
	n-*Butyramide* (M.W. 87·1), 1·405 grams.				iso*Butyramide* (M.W. 87·1), 1·371 grams.		
27·7	0·949	58·1	84·8	23·8	1·068	66·0	85·6
35·8	0·730	45·0	85·8	32·0	0·811	49·2	84·0
44·2	0·593	36·5	85·2	39·2	0·640	40·1	86·8
52·8	0·489	30·6	86·6	47·1	0·531	33·4	87·1
				56·3	0·437	27·9	88·6
	iso*Valeramide* (M.W. 101·1), 1·722 grams.				iso*Butylacetamide* (M.W. 115·1), 1·505 grams.		
23·9	1·213	71·1	94·2	25·8	0·859	50·7	107·7
32·5	0·890	52·4	94·6	33·2	0·645	39·4	111·9
41·8	0·687	40·7	95·2	41·1	0·511	31·8	113·8
50·9	0·556	33·4	96·6	49·4	0·423	26·5	114·4
62·3	0·448	27·4	98·1	57·7	0·358	22·6	115·7
	Glycollamide (M.W. 75·0), 1·330 grams.				*Lactamide* (M.W. 89·1), 1·428 grams.		
27·2	0·982	65·2	79·1	30·6	0·790	52·4	93·9
34·8	0·766	50·9	79·3	38·1	0·649	42·0	91·8
45·1	0·606	39·3	77·4	46·1	0·543	34·7	90·8
54·1	0·493	32·7	79·2	55·6	0·453	28·8	90·1
	Phenylacetamide (M.W. 135·1), 2·302 grams.				*Formanilide* (M.W. 121·1), 2·252 grams.		
29·2	0·942	58·3	133	27·0	1·108	68·8	119·6
39·1	0·711	43·6	132	35·2	0·861	52·8	118·1
48·9	0·566	34·8	132	41·7	0·730	44·6	117·1
57·6	0·475	29·5	134	49·5	0·619	37·5	116·8
67·0	0·409	25·4	134	57·3	0·537	32·4	116·6

Solvent—Alcohol (continued).

Glycollanilide (M.W. 151), 1·895 grams.

V.	Δ.	N_v.	M.W.$_v$
26·1	0·749	48·0	154
33·3	0·600	37·6	151
41·0	0·500	30·6	147
50·5	0·411	24·8	145

Lactanilide (M.W. 165), 2·302 grams.

V.	Δ.	N_v.	M.W.$_v$
26·3	0·865	53·1	161
33·8	0·653	41·2	166
44·7	0·520	31·2	158
54·7	0·413	25·5	162

Urethane (M.W. 89·1), 1·799 grams.

V.	Δ.	N_v.	M.W.$_v$
22·6	1·391	89·4	91·1
29·7	1·049	68·1	91·9
35·2	0·876	57·3	92·7
42·7	0·720	47·2	92·9
49·7	0·615	40·6	93·6
57·3	0·527	35·3	94·6

Phenylurethane (M.W. 165), 2·313 grams.

V.	Δ.	N_v.	M.W.$_v$
25·2	0·870	55·6	168
31·0	0·716	45·1	165
38·1	0·588	36·7	164
45·8	0·494	30·6	162
52·6	0·425	26·7	165

Ethylacetanilide (M.W. 163), 2·327 grams.

V.	Δ.	N_v.	M.W.$_v$
25·2	0·934	56·6	157
32·5	0·719	43·9	158
40·4	0·587	35·3	156
50·0	0·474	28·5	156
60·0	0·400	23·8	154

Phenylcarbamide (M.W. 136·1), 2·678 grams.

V.	Δ.	N_v.	M.W.$_v$
26·0	0·998	75·8	164
32·6	0·803	60·3	162
38·6	0·696	51·0	158
45·5	0·595	43·2	157
51·5	0·533	38·2	155

Diphenylcarbamide (M.W. 212), 1·073 grams.

V.	Δ.	N_v.	M.W.$_v$
58·3	0·149	8·7	196
62·8	0·131	8·0	207

Solvent—Acetone.

Propionamide (M.W. 73·1), 1·238 grams.

V.	W.	Δ.	N_v	M.W.$_v$	M.W.$_w$
24·6	17·83	1·351	68·7	84·4	87·4
31·7	22·93	1·095	53·4	80·7	83·8
41·3	30·16	0·872	40·9	78·0	80·0
50·1	36·81	0·735	33·8	76·3	77·8

Methylacetanilide (M.W. 149), 1·553 grams.

V.	W.	Δ.	N_v	M.W.$_v$	M.W.$_w$
22·8	16·17	1·076	45·6	143	152
29·8	21·42	0·829	34·9	143	149
35·4	25·78	0·692	29·4	144	148
43·8	31·63	0·571	23·8	141	146

Acetamide (M.W. 59), 1·015 grams.

V.	Δ.	N_v.	M.W.$_v$
23·1	1·361	74·3	72·9
29·6	1·135	58·1	68·6
37·7	0·927	45·6	66·0
48·3	0·742	35·6	64·3
55·2	0·667	31·2	62·6

n-*Butyramide* (M.W. 87·1), 1·285 grams.

V.	Δ.	N_v.	M.W.$_v$
25·0	1·204	58·9	96·8
32·0	0·968	46·1	94·2
41·3	0·767	35·7	92·1
52·3	0·612	28·2	91·2

iso*Butyramide* (M.W. 87·1), 1·289 grams.

V.	Δ.	N_v.	M.W.$_v$
21·1	1·337	70·3	103·9
26·3	1·182	56·4	94·2
36·0	0·883	41·1	92·1
43·2	0·740	34·3	91·5
50·9	0·645	29·1	89·6

Valeramide (M.W. 101·1), 1·330 grams.

V.	Δ.	N_v.	M.W.$_v$
26·3	1·081	50·1	106·4
32·0	0·898	41·1	105·2
39·2	0·761	33·5	101·2
46·1	0·656	28·5	99·7

Solvent—Acetone (continued).

iso*Butylacetamide* (M.W. 115·1), 1·784 grams.

V.	Δ.	N_v.	M.W.$_v$.
23·3	1·390	66·5	125
29·5	1·129	52·5	121
38·4	0·880	40·3	120
45·2	0·767	34·3	117

Lactamide (M.W. 89·1), 1·234 grams.

V.	Δ.	N_v.	M.W.$_v$.
27·8	0·902	49·8	111·6
34·4	0·752	40·2	108·1
41·1	0·663	33·7	102·8
47·9	0·594	28·9	98·4

Formanilide (M.W. 121), 1·364 grams.

V.	Δ.	N_v.	M.W.$_v$.
26·3	0·977	42·9	121
33·3	0·767	33·8	121
40·8	0·639	27·6	119
48·0	0·550	23·5	117

Lactanilide (M.W. 165), 2·120 grams.

V.	Δ.	N_v.	M.W.$_v$.
25·6	1·116	50·0	168
32·4	0·900	39·7	165
39·1	0·754	32·9	164
45·5	0·646	28·2	164

Phenylurethane (M.W. 165), 1·905 grams.

V.	Δ.	N_v.	M.W.$_v$.
22·4	1·203	51·4	160
29·9	0·930	38·5	155
37·7	0·731	30·6	157
47·1	0·595	24·5	154

Phenylcarbamide (M.W. 136), 1·288 grams.

V.	Δ.	N_v.	M.W.$_v$.
22·3	0·777	42·4	168
28·0	0·655	33·8	160
34·0	0·563	27·8	152
43·7	0·454	21·7	147

Glycollamide (M.W. 75), 0·472 grams.

V.	Δ.	N_v.	M.W.$_v$.
37·5	0·351	16·8	81·4
46·7	0·307	13·5	74·9
54·5	0·269	11·5	73·1

Phenylacetamide (M.W. 135), 1·809 grams.

V.	Δ.	N_v.	M.W.$_v$.
26·3	1·036	51·0	151
33·2	0·842	40·4	147
39·4	0·714	34·0	146
46·6	0·616	28·8	143

Glycollanilide (M.W. 151), 1·904 grams.

V.	Δ.	N_v.	M.W.$_v$.
27·5	1·013	45·7	155
34·9	0·791	36·1	157
41·1	0·687	30·6	153
49·6	0·568	25·4	153

Urethane (M.W. 89·1), 1·367 grams.

V.	Δ.	N_v.	M.W.$_v$.
31·2	1·072	49·2	92·8
39·1	0·865	39·3	92·0
46·9	0·714	32·7	92·6
57·9	0·560	26·5	95·6

Ethylacetanilide (M.W. 163), 2·000 grams.

V.	Δ.	N_v.	M.W.$_v$.
29·8	0·942	41·1	162
39·1	0·706	31·4	165
48·8	0·569	25·1	163
59·4	0·471	20·6	162

Diphenylcarbamide (M.W. 212), 1·168 grams.

V.	Δ.	N_v.	M.W.$_v$.
41·0	0·294	13·4	220
54·8	0·234	10·0	206

Solvent—Chloroform.

Propionamide (M.W. 73·1), 0·896 gram.

V.	*W.*	Δ.	N_v.	M.W.$_v$.	M.W.$_w$.
19·4	26·6	1·159	63·2	110·4	113·3
26·0	35·1	0·949	47·1	100·5	104·8
32·7	44·2	0·767	37·5	99·0	103·0
40·8	55·2	0·622	30·0	97·7	101·7
48·0	65·7	0·540	25·5	95·7	98·5

Methylacetanilide (M.W. 149), 0·9245 gram.

V.	*W.*	Δ.	N_v.	M.W.$_v$.	M.W.$_w$.
22·2	30·5	0·816	28·0	142	145
28·9	38·7	0·657	21·5	135	142
38·0	51·4	0·491	16·3	137	143
47·6	65·2	0·382	13·0	141	145

Solvent—Chloroform (continued).

Butyramide (M.W. 87), 1·796 grams.

V.	Δ.	N_r.	M.W.$_r$.
34·6	1·245	59·6	115·6
39·0	1·120	52·9	114·0
43·2	1·045	47·8	110·2
47·7	0·950	43·3	110·1
52·6	0·845	39·2	111·8

Valeramide (M.W. 101), 2·115 grams.

V.	Δ.	N_r.	M.W.$_r$.
39·0	1·065	53·7	141
45·7	0·940	45·8	136
52·0	0·825	40·3	137
58·3	0·750	35·9	134
64·9	0·685	32·3	132

Phenylacetamide (M.W. 135), 1·663 grams.

V.	Δ.	N_r.	M.W.$_r$.
39·7	0·695	31·0	167
46·3	0·645	26·6	154
52·4	0·550	23·5	160
60·6	0·475	20·3	160

Glycollanilide (M.W. 151), 2·026 grams.

V.	Δ.	N_r.	M.W.$_r$.
37·5	0·490	35·8	305
44·0	0·480	30·5	266
50·8	0·440	26·4	251
57·3	0·405	23·4	242

Urethane (M.W. 89), 1·617 grams.

V.	Δ.	N_r.	M.W.$_r$.
33·6	1·195	54·1	111·6
39·4	1·030	46·1	110·4
46·3	0·905	39·2	106·9
52·7	0·790	34·4	107·5
58·3	0·685	31·2	112·1

Ethylacetanilide (M.W. 163), 2·218 grams.

V.	Δ.	N_r.	M.W.$_r$.
51·5	0·805	26·4	148
56·9	0·765	23·9	141
62·7	0·715	21·7	137
67·8	0·645	20·1	140·5

iso*Butyramide* (M.W. 87), 1·646 grams.

V.	Δ.	N_r.	M.W.$_r$.
36·0	1·095	52·6	115·6
41·5	0·985	45·6	111·6
47·8	0·870	39·6	109·4
52·9	0·795	35·8	108·3
58·2	0·735	32·5	106·8

iso*Butylacetamide* (M.W. 115), 1·715 grams.

V.	Δ.	N_r.	M.W.$_r$.
47·0	0·645	31·8	157
52·9	0·590	28·2	152
58·5	0·555	25·5	146
64·2	0·490	23·2	151

Formanilide (M.W. 121), 1·430 grams.

V.	Δ.	N_r.	M.W.$_r$.
22·2	1·050	53·2	170
29·2	0·847	40·5	160
35·8	0·680	33·0	163
42·6	0·599	27·7	155

Lactanilide (M.W. 165), 2·125 grams.

V.	Δ.	N_r.	M.W.$_r$.
45·5	0·535	28·3	242
51·6	0·485	25·0	235
57·7	0·450	22·3	227
62·7	0·430	20·5	218
68·8	0·415	18·7	206

Phenylurethane (M.W. 165), 2·284 grams.

V.	Δ.	N_r.	M.W.$_r$.
42·4	0·870	32·7	171·5
48·6	0·745	28·5	175
55·4	0·645	25·0	177
60·0	0·590	23·1	179
65·2	0·555	21·2	175

Solvent—Ether.

Propionamide (M.W. 73·1), 0·3610 gram.

V.	Δ.	N_r.	M.W.$_r$.
38·3	0·325	12·9	89·9
39·8	0·315	12·4	89·3
41·8	0·325	11·8	82·4
43·8	0·330	11·8	77·4

Methylacetanilide (M.W. 149), 1·532 grams.

V.	Δ.	N_r.	M.W.$_r$.
34·7	0·880	29·6	155·5
47·9	0·645	21·5	154
49·4	0·630	20·8	153
50·5	0·620	20·4	152

Solvent—Ether (continued).

*iso*Butylacetamide (M.W. 115), 0·540 gram.

V.	Δ.	N_v.	M.W.$_v$.
40·5	0·265	11·6	156
42·4	0·260	11·1	152
44·5	0·250	10·5	150·5
46·6	0·245	10·1	147
49·0	0·235	9·6	145

Glycollanilide (M.W. 151), 0·5346 gram.

V.	Δ.	N_v.	M.W.$_v$.
36·4	0·275	9·7	165
39·5	0·250	9·0	168
41·8	0·260	8·5	152
43·8	0·245	8·1	154
45·3	0·230	7·8	156

Urethane (M.W. 89·1), 1·013 grams.

V.	Δ.	N_v.	M.W.$_v$.
37·2	0·810	30·6	104·2
39·4	0·765	28·8	104·2
42·0	0·740	27·1	101·0
44·0	0·710	25·8	100·5

Ethylacetanilide (M.W. 163), 2·491 grams.

V.	Δ.	N_v.	M.W.$_v$.
36·4	1·225	42·0	173
38·4	1·180	39·8	170·5
46·6	0·960	32·8	173
48·6	0·940	31·5	169

Formanilide (M.W. 121), 1·052 grams.

V.	Δ.	N_v.	M.W.$_v$.
39·1	0·575	22·2	145
41·4	0·550	21·0	143
43·7	0·530	19·9	141
45·9	0·520	18·9	137
47·9	0·505	18·2	135

Lactanilide (M.W. 165), 1·978 grams.

V.	Δ.	N_v.	M.W.$_v$.
38·4	0·725	31·2	220
39·8	0·705	30·1	219
44·0	0·670	27·2	208
46·5	0·640	25·8	206

Phenylurethane (M.W. 165), 2·940 grams.

V.	Δ.	N_v.	M.W.$_v$.
39·5	1·345	45·1	172
42·9	1·260	41·5	169
51·4	1·040	34·7	170·5
62·0	0·860	28·7	171

Solvent—Benzene.

Propionamide (M.W. 73·1), 0·942 gram.

V.	W.	Δ.	N_v.	M.W.$_v$.	M.W.$_w$.
22·7	17·97	0·854	56·7	155	160
33·4	26·89	0·687	38·5	131	133
45·2	36·37	0·545	28·5	122	124
60·2	48·39	0·446	21·4	112	114

Methylacetanilide (M.W. 149), 1·803 gram.

V.	W.	Δ.	N_v.	M.W.$_v$.	M.W.$_w$.
26·4	20·51	1·483	45·8	147	155
39·2	30·81	0·987	30·8	149	155
52·2	41·36	0·754	23·2	147	151

n-*Butyramide* (M.W. 87·1), 1·288 grams.

V.	Δ.	N_v.	M.W.$_v$.
29·2	0·844	50·7	168
42·7	0·647	34·6	149
57·5	0·523	25·8	137

1·054 grams.

V.	Δ.	N_v.	M.W.$_v$.
27·0	0·764	44·8	163
40·0	0·587	30·3	144
52·8	0·467	22·9	136

*iso*Butyramide (M.W. 87·1), 1·269 grams.

V.	Δ.	N_v.	M.W.$_v$.
29·2	0·842	49·8	165
42·3	0·665	34·4	144
57·9	0·549	25·2	128

0·951 gram.

V.	Δ.	N_v.	M.W.$_v$.
25·0	0·788	43·6	154
37·2	0·605	29·3	135
48·3	0·502	22·6	125

Solvent—Benzene (continued).

Valeramide (M.W. 101·1), 1·432 grams.

V.	Δ.	N_v.	M.W.$_v$.
26·6	0·941	53·2	183
38·4	0·741	36·8	161
51·2	0·602	27·6	149
64·0	0·504	22·1	142

iso*Butylacetamide* (M.W. 115·1), 1·431 grams.

V.	Δ.	N_v.	M.W.$_v$.
28·1	0·851	44·2	191
40·7	0·670	30·5	168
53·7	0·558	23·1	153
65·3	0·475	19·0	148

Formanilide (M.W. 121), 1·435 grams.

V.	Δ.	N_v.	M.W.$_v$.
27·2	1·006	43·5	168
39·5	0·752	30·0	154
53·3	0·597	22·2	144

Glycollanilide (M.W. 151), 1·132 grams.

V.	Δ.	N_v.	M.W.$_v$.
26·0	0·549	28·7	254
37·4	0·451	20·0	215
50·7	0·370	14·8	194
64·2	0·304	11·7	185

Lactanilide (M.W. 165), 1·293 grams.

V.	Δ.	N_v.	M.W.$_v$.
24·1	0·639	32·5	269
36·1	0·498	21·7	230
47·6	0·406	16·4	214
61·0	0·338	12·8	201

Urethane (M.W. 89·1), 1·450 grams.

V.	Δ.	N_v.	M.W.$_v$.
27·8	1·189	58·4	140
41·0	0·852	39·7	133
53·9	0·666	30·2	129

Phenylurethane (M.W. 165), 2·140 grams.

V.	Δ.	N_v.	M.W.$_v$.
26·3	1·514	49·3	172
39·7	1·011	32·7	171
54·1	0·740	23·9	171

Ethylacetanilide (M.W. 163), 2·021 grams.

V.	Δ.	N_v.	M.W.$_v$.
28·7	1·442	43·2	157
44·1	0·940	28·1	156
62·7	0·630	19·8	164

Discussion of Results.

It is not always easy to draw a dividing line between the substances which do and those which do not form associated molecules. We have so far met the difficulty by assuming association to exist where the molecular-weight values exceed the normal by 10 per cent. at the concentration of 30 milligram-molecules per 100 c.c. Our observations were, of course, confined within the solubility limit of the amides, and this limitation is most serious in the case of solutions in ether.

I.—*The Influence of the Solvent in Hindering or Allowing Association of the Solute.*

That a relation exists between the dielectric constant of the solvent and the degree of association of the solute can be seen from the following summary of the results. Those of the previous investigation are included, and are indicated by an asterisk. The dielectric constants ought to be those of the solvents at the boiling point, but we can only quote available data:

Solvent.	Alcohol.	Acetone.	Chloroform.	Ether.	Benzene.
No. of amides investigated ...	$11^{*}+17$	$10^{*}+17$	$9^{*}+13$	$5^{*}+9$	$9^{*}+12$
,, ,, which form simple molecules	24	20	3 and 1 doubtful	3 and 2 doubtful	3 and 1 doubtful
No. of amides which form associated molecules	1 and 3 doubtful	4 and 3 doubtful	18	9	17
Dielectric constant of solvent..	25·4 at 18·5°	21·2 at 22°	5 at 22°	4·4 at 18°	2·3 at 18°

We give the following notes in amplification of the above summary:

1. *Alcohol:* phenylcarbamide is associated, carbamide,* malonamide,* and propionamide * are doubtful.

2. *Acetone:* acetamide,* propionamide, lactamide, and phenylcarbamide are associated, butyramide, *iso*butyramide, and phenylacetamide are doubtful.

3. *Chloroform:* benzanilide,* methylacetanilide, ethylacetanilide, and phenylurethane are unassociated.

4. *Ether:* methylacetanilide, phenylurethane, and ethylacetanilide are unassociated, salicylamide * and glycollanilide are doubtful.

5. *Benzene:* methylacetanilide, ethylacetanilide, and phenylurethane are unassociated, benzanilide * is doubtful.

The fact that alcohol and acetone cannot be regarded absolutely as non-associating solvents is in accordance with the relation which we find to hold between the dielectric constant and the degree of association of the solute. For we should expect a substance which is markedly associated in benzene with a dielectric constant of 2·3 to reveal its tendency to association, although only to a slight and ill-defined extent, in solvents like alcohol and acetone, the dielectric constants of which are 25 and 21 respectively.

As before, we have calculated the molecular weights and association factors at the concentration of 30 milligram-molecules per 100 c.c. in the solvents benzene, ether, and chloroform. The following table includes all our results, those of the previous paper being shown by an asterisk. The older chloroform data have been recalculated, using the new constant (p. 1607).

Propionamide, *iso*butylacetamide, and glycollanilide are not sufficiently soluble in ether to render possible even an estimate of the degree of association at the concentration of 30 milligram-molecules per 100 c.c. There can be no doubt that propionamide and *iso*butylacetamide are associated at the maximum concentration of about 12, and glycollanilide seems to be at 10. Special attention must be drawn to the three substances phenylurethane, methylacetanilide, and ethylacetanilide. They are unassociated in each of the five organic solvents, and might therefore be disregarded, cion has been we prepared to the corre- ound

	Molecular weights in			Associa		
	Benzene.	Ether.	Chloroform.	Benzene.	E	
Acetamide*	—	—	81·5	—	[illegible]	[illegible]
Monochloroacetamide*	130	—	121·5	1·39	—	[illegible]
Dichloroacetamide*	178	160	163	1·39	1·25	1·27
Trichloroacetamide*	210	187	217	1·29	1·15	1·27
Propionamide	124	—	98·8	1·70	(associated)	1·34
n-Butyramide	143	—	110	1·64	—	1·26
*iso*Butyramide	136	—	106	1·56	—	1·22
Valeramide	152	—	130·5	1·53	—	1·29
*iso*Butylacetamide	167	—	154	1·45	(associated)	1·33
Urethane	129	104	105	1·45	1·17	1·18
Phenylurethane	170	170·5	173	1·03	1·03	1·05
Trichlorolactamide*	294	—	—	1·52	—	—
Glycollanilide	258	—	265	1·70	(association doubtful)	1·75
Lactanilide	258	218	243	1·56	1·32	1·47
Formanilide	154·5	164	160	1·27	1·35	1·32
Acetanilide*	205	—	169·5	1·52	—	1·26
Methylacetanilide	149	156	146	1·00	1·04	0·98
Ethylacetanilide	156	171	154	0·96	1·05	0·94
Phenylacetamide	—	—	165	—	—	1·22
Benzamide*	184	—	152	1·52	—	1·26
Benzanilide*	228	—	218	1·17	—	1·10
Salicylamide*	186	—	161	1·36	—	1·17

as having no tendency to association in organic solvents, and therefore as affording no test of the Nernst-Thomson rule. We have preferred to include them, so as to make an underestimate, rather than the opposite, of the extent of agreement with the rule. Even so, our results are sufficient to justify the rule in the case of organic solvents.

II.—*The Constitution of the Amide and the Extent of Association.*

With the data we have now collected we are able to illustrate the influence of constitution on the tendency of the amide to form associated molecules. This tendency is shown to the greatest extent in benzene solution, and the data presented above, showing the degree of association at a certain concentration, allow of the following deductions:

(1) The molecules of the aliphatic amides are strongly associated, and (2), as is known to be the case in the homologous series of acids and alcohols, the extent of association decreases with increasing molecular weight. (3) The phenyl group depresses the tendency to association; thus, not only are the aromatic amides associated to a smaller extent than the aliphatic, but the anilide is less strongly associated than the corresponding amide, and phenylurethane much less than urethane. (4) The substitution of both hydrogen atoms of the amide, as in methyl- and ethyl-acetanilide, yields a substance of normal molecular size.

To consider the converse of the matter, we cannot think that

, Solv of molecular complexity can settle questions of
No. of amides in itution. No one maintains now that the hydroxyl
" " ple molec w only cause of association, and that the amides
ich show a tendency to association have therefore the hydroxylic constitution. That hypothesis regarding the amides, as the sole explanation of the phenomena, was refuted first by Auwers (*Zeitsch. physikal. Chem.*, 1899, **30**, 541, 542). But the suggestion which he made then, that the tervalent nitrogen atom may have as much to do with the association of amides as the hydroxyl group, is not confirmed by our observations regarding methyl- and ethyl-acetanilide. These substances show no tendency to association in organic solvents, whilst acetanilide is associated in benzene, chloroform, and ether. These facts are sufficient to illustrate the difficulty of tracing all the complexities of this problem.

The materials used in this investigation were obtained by means of grants from the Government Grant Committee of the Royal Society and the Executive Committee of the Carnegie Trust for the Universities of Scotland.

THE UNIVERSITY,
MANCHESTER.

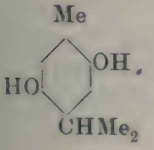
THE UNIVERSITY,
SHEFFIELD.

CL.—*Contributions to the Chemistry of the Terpenes. Part VII. Synthesis of a Monocyclic Terpene from Thymol.*

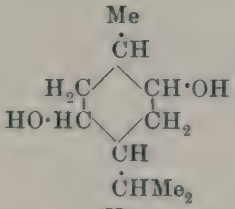
By GEORGE GERALD HENDERSON and MAGGIE MILLEN JEFFS SUTHERLAND, B.Sc. (Carnegie Research Scholar).

SEVERAL monohydric alcohols of the *cyclo*hexane series have already been prepared by the hydrogenation of monohydric phenols in presence of nickel according to Sabatier and Senderens's method, but, so far as we are aware, the reaction has not hitherto been extended to any dihydric phenol. It appeared of interest to investigate the behaviour of a dihydric phenol of the formula $C_{10}H_{12}(OH)_2$ when heated to the requisite temperature with hydrogen in the presence of finely divided nickel, in the hope that it would unite additively with hydrogen and yield a dihydroxymenthane of the formula $C_{10}H_{18}(OH)_2$, and that from this glycol we could obtain a monocyclic terpene, one of the menthadienes, by elimination of the elements of water. This expectation has been realised. Starting with thymol (3-hydroxycymene), we prepared 6-nitrosothymol (thymoquinoneoxime), reduced this to the corresponding amino-derivative, oxidised the latter to thymoquinone, and by reduction of the thymoquinone with sulphurous acid obtained thymoquinol, $C_{10}H_{12}(OH)_2$. This dihydric phenol was found to be susceptible of direct hydrogenation by the method of Sabatier and Senderens, and gave the desired product, *menthane*-2 : 5-*diol*, $C_{10}H_{18}(OH)_2$. Finally, when the glycol so prepared was heated with potassium hydrogen sulphate, it lost the elements of 2 molecules of water, and yielded an unsaturated *hydrocarbon* of the formula $C_{10}H_{16}$, which exhibited the properties of a monocyclic terpene.

Considering its relationship to thymoquinol (formula I), it is clear that the dihydroxymenthane must have the constitution represented in formula II. The terpene derived from the dihydroxymenthane should contain two ethylenic linkings in the ring, or, in other words, should be isomeric with α-terpinene. Probably it is either $\Delta^{1:4}$- (formula III) or $\Delta^{2:5}$-menthadiene (formula IV). The quantity of the terpene at our disposal did not permit of experiments being instituted to determine the relative positions of the double bonds, but we hope to be able to examine it more fully later.



(I.)



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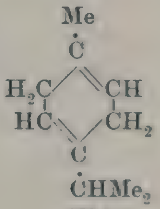

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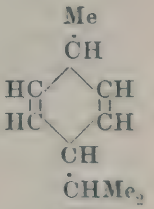

(IV.)

EXPERIMENTAL.

Preparation of Menthane-2 : 5-*diol*.—6-Nitrosothymol was obtained by Klages' method (*Ber.*, 1899, **32**, 1518), which gave very satisfactory results. The 6-nitrosothymol was then converted into thymoquinone in the following manner. Twenty-five grams of the nitroso-compound were dissolved in 250 c.c. of 10 per cent. aqueous ammonia, and the solution was saturated with hydrogen sulphide. The precipitate of 6-aminothymol, which separated, was collected, washed with water, and dissolved in 450 c.c. of 3 per cent. sulphuric acid, and to the solution 500 c.c. of water and 250 c.c. of a 10 per cent. solution of potassium dichromate were added. After about half an hour the precipitate which had formed was collected, and dissolved in ten times its weight of glacial acetic acid. Chromic anhydride was added to this solution in small quantities at a time until the oxidation was completed, and the thymoquinone was then precipitated by addition of water, collected, and dried. The yellow crystals of the quinone melted at 45°.

From the thymoquinone the corresponding quinol was prepared by reduction with sulphurous acid, as described by Carstanjen (*J. pr. Chem.*, 1871, [ii], **3**, 50), and the following method was adopted for its hydrogenation. A long combustion tube, containing finely divided nickel, which was prepared by reducing the pure oxide, in a fine state of division, with hydrogen at as low a temperature as possible, was heated in an air-bath, a porcelain boat containing the substance was placed in the front part, and a fairly rapid current of hydrogen was passed through the tube. The hydrogen, of course, was carefully purified and dried. A number of preliminary experiments had shown that the most favourable temperature for the hydrogenation of the quinol was 190—200°, and accordingly the temperature of the tube was maintained at that point. Under these conditions an extremely viscous liquid slowly distilled from the tube, and was collected in a cooled receiver to which a **U**-tube filled with glass wool was attached. At first the distillate was quite colourless, but the last portion which passed over had a brown tinge. When the distillate was kept in the ice-chest, crystals began to form, but the process was very slow. The viscous liquid was therefore stirred with a small quantity of benzene, with the result that the greater part of it quickly became crystalline. The crystals were drained from a small proportion of an oily substance with which they were mixed, and recrystallised several times from benzene. The purified product was analysed, and found to be the desired dihydroxymenthane:

0·1262 gave 0·3210 CO_2 and 0·1322 H_2O. C = 69·4; H = 11·6.
0·1240 „ 0·3160 CO_2 „ 0·1310 H_2O. C = 69·5; H = 11·7.
$C_{10}H_{20}O_2$ requires C = 69·8; H = 11·6 per cent.

Menthane-2:5-*diol*, $C_{10}H_{18}(OH)_2$, crystallises from benzene in very small, colourless plates, which melt at 112°. When dry, it has the form of a white powder, and it has no odour. It is very readily soluble in alcohol, ether, light petroleum, or hot benzene, and readily so in cold benzene. Hot water dissolves it sparingly, cold water scarcely at all. It distils without decomposition under diminished pressure (b. p. about 155°/15 mm.), or in a current of hydrogen at the ordinary pressure.

The small quantity of an oily substance which was separated from the crystalline menthane-2:5-diol during the process of purification was collected and fractionally distilled under diminished pressure in an atmosphere of dry carbon dioxide. Under 15 mm.

pressure a small fraction distilled at 80—100°, a still smaller fraction at 100—140°, and the bulk at 150—160°. The highest fraction solidified on cooling, and was found to consist almost wholly of menthane-2:5-diol. The fraction which distilled at 80—100° was too small in quantity to permit of satisfactory purification, but when treated with semicarbazide hydrochloride and potassium acetate in the usual manner it yielded a little of a crystalline solid. When purified by crystallisation from alcohol, in which it is very sparingly soluble, this compound forms small crystals, which are almost colourless, and melt and decompose at 243—244°. It is almost insoluble in water or ether. From an analysis, of which the result is quoted below, it appears not improbable that the compound is the disemicarbazone of a diketone of the formula $C_{10}H_{16}O_2$, derived from the disecondary alcohol, menthane-2:5-diol:

0·1132 gave 29 c.c. N_2 at 18° and 748 mm. $N=29·2$.

$C_{12}H_{22}O_2N_6$ requires $N=29·6$ per cent.

Preparation of a Menthadiene from Menthane-2:5-diol.—An intimate mixture of menthane-2:5-diol with twice its weight of dry powdered potassium hydrogen sulphate was placed in a flask attached to a reflux condenser, and heated in a bath of fusible metal. When the temperature of the bath approached 190° a vigorous reaction began, and a colourless liquid vaporised and condensed in the tube. After having been heated for about half an hour at 190—200°, the mixture was cooled and distilled in a current of steam. A mobile, colourless liquid distilled with the steam and floated on the surface of the water in the receiver. The liquid was extracted with ether, the ethereal solution dried, the ether removed by distillation, and the residual liquid again mixed with potassium hydrogen sulphate and heated as before. The resulting mixture was distilled in a current of steam, the liquid extracted from the distillate with ether, the ethereal solution dried, and the ether distilled off. The liquid remaining in the flask was repeatedly distilled over sodium until no sign of any reaction could be observed, and finally we obtained a small quantity of a substance of practically constant boiling point, which analysis showed to have the composition of a terpene:

0·1540 gave 0·4963 CO_2 and 0·1636 H_2O. $C=87·9$; $H=11·8$.
0·2897 „ 0·9358 CO_2 „ 0·3024 H_2O. $C=88·1$; $H=11·6$.

$C_{10}H_{16}$ requires $C=88·2$; $H=11·8$ per cent.

The *terpene* thus obtained is, as already stated, probably one of the isomeric terpinenes not hitherto described. It is colourless, has a rather faint odour somewhat like that of limonene, and a characteristic burning taste like oil of turpentine. Its boiling point is 179°/760 mm.; $n_D^{20} = 1·4779$; the specific gravity is somewhat greater than 0·84, but the quantity of the substance available was too small for an exact determination, especially as it appears to polymerise on keeping. It is practically insoluble in water, but dissolves in the usual organic solvents. It at once decolorises a dilute alkaline solution of potassium permanganate. When mixed with a solution of dry bromine in dry chloroform, it instantly unites with the bromine to form an additive compound, but the product must be unstable under the conditions of the experiment, since when rather more than three atomic proportions of bromine had been added, evolution of hydrogen bromide began. When treated with nitrous acid according to Wallach's method, the liquid turns yellow, but no crystalline nitrosite could be isolated. We hope to be able to complete the examination of this terpene before long.

It is our intention to endeavour to obtain terpenes from other monohydric phenols isomeric with thymol on the lines indicated in this paper.

We are indebted to the Research Fund Committee of the Carnegie Trust for a grant which defrayed the expense of this work.

CHEMISTRY DEPARTMENT,
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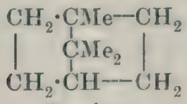
CLI.—*Contributions to the Chemistry of the Terpenes. Part VIII. Dihydrocamphene and Dihydrobornylene.*

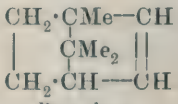
By GEORGE GERALD HENDERSON and ERNEST FERGUSON POLLOCK.

ACCORDING to the view now generally accepted as the most probable one, the arrangement of the carbon atoms in the molecule of bornylene is the same as in that of the saturated hydrocarbon camphane, whilst the structure of the molecule of camphene is of a different type, as is shown in the following formulæ:



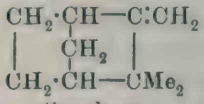
$$\begin{array}{l}CH_2{\cdot}CMe{-}CH_2\\ |\quad CMe_2\quad |\\ CH_2{\cdot}CH{-}CH_2\end{array}$$

Camphane.



$$\begin{array}{l}CH_2{\cdot}CMe{-}CH\\ |\quad CMe_2\quad \|\\ CH_2{\cdot}CH{-}CH\end{array}$$

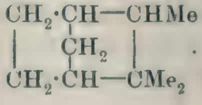
Bornylene.



$$\begin{array}{l}CH_2{\cdot}CH{-}C{:}CH_2\\ |\quad CH_2\quad |\\ CH_2{\cdot}CH{-}CMe_2\end{array}$$

Camphene.

If this conception of the molecular structure of these hydrocarbons be correct, it follows that dihydrobornylene, $C_{10}H_{18}$, should be identical with camphane, and that dihydrocamphene, $C_{10}H_{18}$, should have the constitution shown in the formula



$$\begin{array}{l}CH_2{\cdot}CH{-}CHMe\\ |\quad CH_2\quad |\\ CH_2{\cdot}CH{-}CMe_2\end{array}.$$

We have recently carried out a number of experiments with the object of throwing light on this point, and have ascertained that, in accordance with theory, when bornylene is hydrogenated, camphane is produced, and that camphene yields a dihydro-compound which is certainly not camphane.

The preparation of *dihydrobornylene* has not hitherto been described, but we have found that it can be obtained easily from bornylene by the application of Sabatier and Senderens' method. The bornylene used in our experiments was prepared from borneol, through methyl bornyl xanthate, according to the very satisfactory process of Tschugaeff (*Ber.*, 1899, **32**, 3332); it melted at 103°, boiled at 149—150°, and was optically inactive. A porcelain boat containing bornylene was placed in the front part of a long tube containing finely divided nickel, which was prepared by reducing pure nickel oxide with hydrogen at the lowest possible temperature, and a current of carefully purified and dried hydrogen was passed at such a rate that from 2 to 3 grams of bornylene were carried through the tube in one hour. The tube was maintained by means of an air-bath at a temperature of 170—190°, which preliminary experiments had shown to be the most favourable one, and the solid dihydrobornylene which passed over was collected in a cooled receiver. Hydrogenation took place readily, and the product contained little or no unchanged bornylene; it was finally purified by crystallisation from methyl alcohol. The dihydrobornylene so prepared separates from methyl alcohol in small, white crystals, which have a faint odour somewhat like that of borneol. It melts at 150°, boils at 161—162° under the ordinary pressure, and sublimes easily, forming colourless, lustrous crystals. When treated with bromine and with potassium permanganate, it shows the character of a saturated hydrocarbon. In all these respects dihydrobornylene is exactly similar to camphane, and there can be no doubt as to their identity.

Dihydrocamphene has already been described by several observers, but their statements are somewhat contradictory. By heating *iso*borneol with zinc dust for a short time at 220°, Semmler (*Ber.*, 1900, **33**, 776) obtained a hydrocarbon, $C_{10}H_{18}$, which boiled at 162°, and separated from alcohol in fern-like aggregates of crystals, of which the melting point was 85°. This hydrocarbon was probably dihydrocamphene. Sabatier and Senderens (*Compt. rend.*, 1901, **132**, 1254) applied their method of hydrogenation in presence of nickel to camphene, and obtained a liquid hydrocarbon of the formula $C_{10}H_{18}$, which boiled at 164—165°. Finally, Vavon (*Compt. rend.*, 1909, **149**, 997) found that camphene in ethereal solution absorbs hydrogen when agitated with platinum black, and yields a solid compound, $C_{10}H_{18}$, which is similar to camphene in appearance, but melts at 87°.

Using the same arrangement as in the case of bornylene, we examined the action of hydrogen on camphene in presence of heated nickel, and found in the first place that under these conditions camphene does not unite with hydrogen either so easily or so completely as bornylene. The camphene which we employed melted at 54°, and boiled at 160°. A number of observations were made at different temperatures, and in some cases the product was passed a second or even a third time through the heated tube. The results of numerous experiments may be summarised as follows. At temperatures ranging from 120° to 180° the product was a solid, resembling camphene in appearance, but melting at about 64°. At a temperature of 200—220°, the product was a mixture of a solid with a colourless liquid. At about 240° the product was a colourless, somewhat viscous liquid—in all probability the same substance as was obtained by Sabatier and Senderens. The solid product, melting at 64°, when tested with bromine gave evidence of the presence of a small proportion of an unsaturated hydrocarbon. It was subjected to repeated fractional crystallisation from methyl alcohol, and was ultimately proved to be a mixture of the dihydrocamphene described by Vavon with a little unchanged camphene. The liquid product formed at 240° was also found, by means of bromine, to contain a little of an unsaturated substance. When cooled in the ice-chest, it gradually solidified, and on subsequent exposure to the ordinary temperature part remained solid, while the other part became liquid again. The liquid part was poured off and again cooled, and then kept at the ordinary temperature, when a further yield of the solid was obtained. Finally, by frequent repetition of this procedure, almost the whole of the original liquid was obtained in solid form. The solid was ultimately separated by repeated fractional crystallisation from methyl alcohol into the dihydrocamphene of Vavon and a little unchanged camphene. It was thus shown that the liquid which we obtained by the hydrogenation of camphene according to Sabatier and Senderens' method is a mixture of dihydrocamphene with some unchanged camphene and a little of a third substance which was not further investigated. The dihydrocamphene obtained is saturated towards bromine or towards potassium permanganate, but it has a melting point widely different from that of camphane, is quite unlike it in appearance, and is undoubtedly a different substance.

We are indebted to the Research Fund Committee of the Carnegie Trust for a grant which defrayed the expense of this work.

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CLII.—*The Chlorination of Toluene.*

By JULIUS BEREND COHEN, HARRY MEDFORTH DAWSON, JOHN REGINALD BLOCKEY, and ARNOLD WOODMANSEY.

A PRELIMINARY note on the above subject was published in 1905 (Trans., **87**, 1034), and in this an account was given of the action of chlorine obtained by the electrolysis of aqueous hydrochloric acid in contact with boiling toluene. The results pointed to a marked difference in the products so obtained from those which are produced by the action of ordinary chlorine under similar conditions.

During the course of further experiments it has been found that diffused daylight acts so rapidly in producing side-chain substitution that comparable results are only possible when light is rigidly excluded. On this account the comparative experiments described in this paper were carried out in the dark. In the second place, a much more rapid and accurate process for estimating the amount of the side-chain and nuclear substitution products was used in place of the former analytical method.

While these experiments were in progress several papers dealing with the closely related question of the bromination of toluene have appeared, and a review of the subject of the chlorination and bromination of benzene and toluene has been published by Bancroft in the third of a series of articles on "The Electrochemistry of Light" (*J. Physical Chem.*, 1908, **12**, 420).

When chlorine acts on toluene, side-chain substitution takes place (1) in sunlight at 0° and higher temperatures (Schramm, *Ber.*, 1885, **18**, 606); (2) in the dark at the boiling point of toluene (Cannizzaro, *Compt. rend.*, 1855, **41**, 517). According to Häussermann and Beck (*Ber.*, 1892, **25**, 2445), side-chain substitution is greatly facilitated in the case of nitrotoluene in presence of sulphur. Sulphur thus appears to behave differently from the usual carriers, such as ferric chloride, molybdenum pentachloride, antimony pentachloride, iodine chloride, pyridine, and the aluminium-mercury couple, for these bring about nuclear substitution.

In contrast with the qualitative nature of the observations relating to the process of chlorination, quantitative measurements showing the influence of various factors on the side-chain and nuclear substitution have been obtained in connexion with the bromination of toluene. The experiments of Holleman, Polak, van der Laan, and Euwes (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 512; *Rec. trav. chim.*, 1908, **27**, 435), and those of Bruner and Dluska (*Bull. Acad. Sci. Cracow*, 1907, 693) have shown that the relative proportion of bromine which enters the side-chain is not only increased by light, but in the dark it is increased by rise of temperature and by dilution of the reacting bromine. The methods adopted in these two series of experiments were not the same, for whereas Holleman and his collaborators used open vessels and only analysed the product obtained when the bromine had completely disappeared, Bruner and Dluska employed sealed tubes and analysed the products at different stages of the reaction.

The influence of the nature of the medium on the distribution of the bromine between the side-chain and the nucleus was also examined by these authors. When the toluene is considerably diluted by admixture with carbon tetrachloride, this distribution is the same as in the case of pure toluene, but dilution to the same extent with nitrobenzene has the effect of decreasing the proportion of the bromine which enters the toluene side-chain. This influence of the medium has been further studied by Bruner and Vorbrodt (*Bull. Acad. Sci. Cracow*, 1909, 221), who investigated the effect of carbon disulphide, carbon tetrachloride, benzene, chloroform, acetic acid, benzonitrile, and nitrobenzene on the bromination of toluene, ethylbenzene, *iso*propylbenzene, and *o*-, *m*-, and *p*-xylene. They find that the influence of the solvent is not only observable in the dark, but shows itself in the process of photobromination. The effect of nitrobenzene, and to a less extent of acetic acid and benzonitrile, is greatly to diminish the proportion of side-chain substitution.

With regard to the bromination of toluene in the presence of carriers, Bruner and Holleman (*loc. cit.*) and Jackson and Field (*Amer. Chem. J.*, 1881, **2**, 10) have found that side-chain substitution increases with decreasing concentration of the carrier and also with rise of temperature.

In explanation of these various observations, two essentially different views have been put forward. According to Bruner, side-chain substitution is due to molecular bromine, whereas nuclear substitution is effected by bromine atoms or ions, which result from the dissociation of bromine molecules in accordance with the equation:

$$\mathrm{Br_2} \rightleftharpoons \mathrm{Br} + \mathrm{Br}.$$

The velocity measurements of Bruner and Dluska are cited as evidence in favour of this hypothesis. These determinations indicate that both the side-chain and nuclear substitution processes take place in accordance with the requirements of the equation for a unimolecular change if the concentration of the bromine is small. For higher bromine concentrations, the values obtained for the constant characteristic of a unimolecular change decrease as the reaction proceeds. This is attributed to the withdrawal of active bromine from the solution by the formation of a hydrogen perbromide (HBr_3). Since the dissociation of this perbromide increases as the concentration of the solution diminishes, its influence on the rate of progress of the bromination is inappreciable in the case of dilute bromine solutions.

According to this hypothesis, the action of carriers, such as iodine, consists in forming compounds with bromine which undergo dissociation with the production of bromine atoms or ions in much greater concentration than that which is obtained in the case of a pure solution of bromine. Hydrogen perbromide is supposed to be a dissociating compound of this character, and the increase in the proportion of nuclear substitution which is found when the toluene is mixed with nitrobenzene, benzonitrile, acetic acid, and certain other liquids, is attributed to the relatively large solubility of hydrogen bromide in these solvents, whereby the formation of hydrogen perbromides is facilitated.

Bruner's theory that nuclear substitution is due to ionic bromine is in the main adopted by Bancroft (*loc. cit.*). To account for certain observations, this author finds it necessary, however, to assume that nuclear substitution only occurs when negative bromine ions are present in excess of the corresponding positive ions. Such a condition is brought about by the partial combination of the positive bromine ions with molecular bromine to form complex positive ions, for example, Br_3.

The other view referred to is that put forward by Holleman, who supposes that side-chain substitution is due to molecular bromine, but that substitution in the nucleus is brought about by bromine in the form of hydrogen perbromide, HBr_n. Low temperature and increasing concentration of the solution are favourable to the formation of these polyhalogen compounds, and these are the conditions under which the proportion of nuclear substituted product increases. The fact that nitrobenzene and acetic acid, when added to the toluene, increase the relative amount of the nuclear substitution product, is obviously in agreement with this theory if the solubility relationships, referred to above, are taken into consideration.

An account will now be given of the observations which we have made in connexion with the chlorination of toluene, and the method of analysis of the chlorinated product may be described first.

This product consists of unchanged toluene, *o*- and *p*-chlorotoluene, and benzyl chloride. The benzyl chloride was extracted by Schultze's method (*Ber.*, 1884, **17**, 1675), which consists in boiling a weighed quantity of the liquid with an excess of alcoholic silver nitrate for fifteen to twenty minutes, and weighing the silver chloride. The method was tested with pure benzyl chloride and with benzyl chloride mixed with toluene and *o*- and *p*-chlorotoluene. The following results show that the method of estimation is satisfactory:

0·2618 benzyl chloride gave 0·2983 AgCl; $C_6H_5{\cdot}CH_2Cl = 0{\cdot}2630$.
0·8220 ,, ,, ,, 0·9192 AgCl; $C_6H_5{\cdot}CH_2Cl = 0{\cdot}8112$.

The following mixtures were made and analysed:

	I.	II.	III.
Toluene	26·026	3·523	6·459
o-Chlorotoluene	9·328	1·329	4·8765
p-Chlorotoluene	5·306	1·267	2·0575
Benzyl chloride	4·845	2·103	2·3685

I. 6·2013 gave 0·7055 AgCl; $C_6H_5{\cdot}CH_2Cl = 10{\cdot}04$. Actual = 10·54 per cent.
II. 3·0554 ,, 0·8815 AgCl; $C_6H_5{\cdot}CH_2Cl = 25{\cdot}46$. ,, = 25·61 ,,
III. 3·4065 ,, 0·5870 AgCl; $C_6H_5{\cdot}CH_2Cl = 15{\cdot}21$. ,, = 15·03 ,,

The proportion of *p*-chlorotoluene in the mixture was estimated by oxidising the chlorinated product in a sealed tube at 115—120° for five to six hours with nitric acid (one part of acid, D 1·4, and two parts of water). The mixture of acids was collected and washed with cold water. The acids were then boiled with 200 c.c. of water for a few minutes, filtered hot, and washed with a small quantity of boiling water. All the benzoic and *o*-chlorobenzoic acid and a small quantity of *p*-chlorobenzoic acid are thus removed. It was found that one litre of boiling water dissolves about 1·0 gram of *p*-chlorobenzoic acid, so that a loss of approximately 0·20 gram of this acid has to be allowed for in the above method of separation. After washing as described, the acid was dried at 100° and weighed. The melting point of the acid was 234—235°. In carrying out this estimation of the *p*-chlorotoluene, it is necessary to keep the temperature at which the oxidation is effected as low as possible, for otherwise a portion of the *p*-chlorobenzoic acid may be decomposed. Mixtures of the following percentage composition were analysed by the above method:

	I.	II.
Toluene	19·16	15·73
o-Chlorotoluene	43·54	43·07
p-Chlorotoluene	19·40	20·92
Benzyl chloride	17·90	20·28

I. 2·77 gave 0·695 *p* chlorobenzoic acid. *p*-Chlorotoluene = 20·3 per cent.
II. 3·42 ,, 0·880 ,, ,, ,, = 20·8 ,,

In some of the earlier experiments, the total chlorine was determined by the Carius method. By deducting from this the chlorine present as benzyl chloride and *p*-chlorotoluene, the amount of *o*-chlorotoluene was obtained. In the later experiments this method was replaced by a simpler and more rapid process involving the measurement of the density of the chlorinated product. If α, β, γ, and δ are the percentage amounts of toluene, *o*-chlorotoluene, *p*-chlorotoluene, and benzyl chloride respectively in a mixture of these substances, and if d_1, d_2, d_3, and d_4 are the respective densities of these liquids (at 18°), we may obtain α and β from the equations:

$$\alpha+\beta=100-\gamma-\delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

$$\frac{\alpha}{d_1}+\frac{\beta}{d_2}=\frac{100}{d}-\frac{\gamma}{d_3}-\frac{\delta}{d_4} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

in which d represents the density of the mixture. This method was applied in the analysis of the following mixtures:

		Percentage composition.		
		I.	II.	III.
Toluene	($d_1=0{\cdot}86791$)	$\alpha=19{\cdot}90$	19·16	15·73
o-Chlorotoluene	($d_2=1{\cdot}08480$)	$\beta=30{\cdot}90$	43·54	43·07
p-Chlorotoluene	($d_3=1{\cdot}07050$)	$\gamma=18{\cdot}64$	19·40	20·92
Benzyl chloride	($d_4=1{\cdot}10271$)	$\delta=30{\cdot}56$	17·90	20·28
Density of mixture		$d_0^{18}=$ 1·03615	1·03584	1·04414
Calculated value of α (per cent.)		19·8	19·0	15·7

In calculating the above values of α, the actual percentage amounts of *p*-chlorotoluene and benzyl chloride were assumed.

Having subsequently ascertained that the ratio of *p*- to *o*-chlorotoluene in the product of chlorination is nearly constant and equal to 1 : 2, the separate estimation of the para-compound was omitted in further experiments, and the total amount of the nuclear substitution product (*o*- + *p*-chlorotoluene) was alone determined. The density of a mixture of the two chlorotoluenes in the above ratio was found to be $d_0^{18}=1{\cdot}0800$. From this and the measured density, d, of a given mixture, we obtain the percentage amounts of toluene (α) and of the mixed chlorotoluenes ($\beta+\gamma$) from the equations:

$$\alpha+(\beta+\gamma)=100-\delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

$$\frac{\alpha}{0{\cdot}86791}+\frac{(\beta+\gamma)}{1{\cdot}0800}=\frac{100}{d}-\frac{\delta}{1{\cdot}10271} \quad . \quad . \quad . \quad . \quad (4).$$

The results obtained for a mixture of known composition by this method are indicated below:

	Percentage composition.
Toluene	α = 92·20
o- and *p* Chlorotoluenes	$(\beta+\gamma)=$ 3·75
Benzyl chloride	δ = 4·05
Density of mixture	d = 0·88250

1·8695 of the mixture gave 0·0868 AgCl, corresponding with $\delta=4{\cdot}10$ per cent. of benzyl chloride. Substituting for δ and d in equations (3) and (4), we obtained $\alpha=91{\cdot}9$, $(\beta+\gamma)=4{\cdot}0$ per cent. This example suffices to show that sufficiently accurate results for the proportion of total nuclear substitution product in the mixture can be obtained by the indirect method of density determination. Previous to the carrying out of the above estimations, the chlorinated mixture was washed with a solution of sodium carbonate until the wash-water, acidified with nitric acid, gave no precipitate with silver nitrate solution. It was then dried over potassium carbonate.

Variations in the Conditions of the Chlorination Process.—In order to ascertain the influence of various factors on the distribution of the chlorine between the side-chain and the nucleus, the following series of experiments were made, the toluene in all cases being heated at its boiling point during the process of chlorination.

Series I *and* II.—Chlorination above a layer of hydrochloric acid solution (D 1·16) in the dark and in diffused daylight.

Series III *and* IV.—Chlorination with moist chlorine in the dark and in diffused daylight.

Series V *and* VI.—Chlorination with dry chlorine in the dark and in diffused daylight.

In the last four series of experiments hydrogen chloride was passed into the toluene with the chlorine, so as to make the conditions correspond as closely as possible with those of series I and II. In the experiments of series V and VI, the gases were passed through concentrated sulphuric acid and then over phosphoric oxide, and the toluene was freshly distilled over sodium.

The results of these experiments are given in table I, in which the last two columns of numbers represent respectively the percentage amounts of chlorine which enter the side-chain and the nucleus. The figures in the third column indicate the extent to which the chlorination was carried in the separate experiments. From a comparison of the individual results in the different series, it would appear that in some cases the distribution of the chlorine between side-chain and nucleus is to some extent dependent on the proportion of the toluene which is actually chlorinated. The variations are, however, not such as to permit of any definite conclusion in regard to this point, and we have considered it permissible to take the mean results of the separate experiments.

TABLE I.

Chlorination with Ordinary Chlorine.

Series.	Conditions.	Percentage of substitution products in final mixture.	Percentage of	
			Benzyl chloride.	*o*- + *p*-Chloro-toluenes.
I. *a*	Layer of hydrochloric acid solution in the dark.	10	16	84
b		10	14·5	85·5
c		10	19	81
d		9	16	84
e		9	17	83
f		9	24	76
g		11	13·5	86·5
h		13	12·5	87·5
	Mean	....	16·5	83·5
II.	Layer of hydrochloric acid solution in the light.	17	64	36
		40	59	41
		48	56	44
	Mean	....	60	40
III.	Moist chlorine and hydrogen chloride in the dark.	12	63	37
		18	46	54
		8	76	24
		9	64	36
	Mean	....	62	38
IV.	Moist chlorine and hydrogen chloride in the light.	50	91	9
		35	90	10
	Mean	....	90	10
V.	Dry chlorine and hydrogen chloride in the dark.	29	91	9
		25	90	10
	Mean	....	90	10
VI.	Dry chlorine and hydrogen chloride in the light.	22	93·5	6·5
		44	94	6
	Mean	....	94	6

In reference to the experiments in series I, certain slight modifications were made in the experimental arrangement in order to ascertain whether the substituting effect of chlorine is influenced by previous exposure to light. In *a* and *b* the chlorine was exposed to the light of an arc lamp, focussed on the wash-bottle containing sulphuric acid, before it came into contact with the toluene. In *c*, *d*, *e*, and *f*, the chlorine was exposed to diffused daylight, the only difference being that in *e* the sulphuric acid in the wash-bottle was replaced by water. In *g* and *h*, the light of an ordinary incandescent electric lamp was allowed to act on the chlorine before it entered the toluene. Although the results of the several experiments vary to some extent, it is not possible to say that the previous light treatment of the chlorine has any definite influence on the proportion of the side-chain substitution.

Before proceeding to compare the data in table I, it will be convenient to present the results of the experiments in which chlorination was effected by chlorine generated by electrolytic decomposition of a concentrated hydrochloric acid solution placed immediately below the toluene. The apparatus used was that described in the previous communication (*loc. cit.*), and, as in the other experiments, the temperature was maintained at the boiling point of toluene.

TABLE II.

Chlorination with Electrolytic Chlorine.

				Percentage of	
Series.	Conditions.		Percentage of substitution products in final mixture.	Benzyl chloride.	o- + p-Chloro-toluenes.
VII.	In the dark	0·5 amps., 8 hours	9	9·5	90·5
		0·5 ,, 24 ,,	3·5	5·5	94·5
		1 ,, 4 ,,	4	11·5	88·5
		1 ,, 4 ,,	7	8·5	91·5
		4 ,, 1 ,,	10	14·0	86·0
		4 ,, 2 ,,	24	12·0	88·0
			Mean...........	10·0	90·0
VIII.	In the light	1 amp., 4 hours	15	59·0	41·0
		1 ,, 4 ,,	14	69·0	31·0
			Mean...........	64·0	36·0

Examination of table I shows that the influence of light on the ratio of distribution of the chlorine is very pronounced in the case where the reacting chlorine was passed through concentrated aqueous hydrochloric acid in contact with the toluene. The effect of insolation is to raise the proportion of chlorine which enters the side-chain from about 16 to 60 per cent. In the case where the moist gases were passed directly into the toluene, the effect of light is to raise the percentage of benzyl chloride from about 60 to 90. When, however, the dry gases are passed into dry toluene, the proportion of side-chain substitution product obtained in the dark is already so large that any considerable influence of light is impossible. As the numbers show, the effect of light in this case is very slight, the proportion of benzyl chloride being increased from 90 to 94 per cent.

If we compare series I, III, and V, which were all carried out in the dark, it is seen that the distribution of the chlorine is very largely dependent on the amount of water present. In the absence of water, the proportion of benzyl chloride amounts to 90 per cent.; when the chlorine and hydrogen chloride were not dried before passing into the toluene, the mean of the divergent numbers obtained for the proportion of benzyl chloride is only 62 per cent., and when the toluene undergoing chlorination was saturated with water by contact with aqueous hydrochloric acid, the proportion of benzyl chloride is only 16 per cent. The considerable differences in the numbers for the separate experiments of series III may be due to the different amounts of moisture which were introduced by the undried gases in the different experiments.

The data obtained with electrolytic chlorine in the dark (series VII) must be compared with those of series I. The special arrangement adopted in this series was in fact designed to make the conditions as similar as possible to those which obtained in the process of electrolytic chlorination, and thereby to facilitate a comparison of the action of ordinary and electrolytic chlorine. The mean results of the two series are not identical, and it would appear that electrolytic chlorine gives rise to a somewhat smaller proportion of benzyl chloride than chlorine, which is obtained by the action of potassium permanganate on hydrochloric acid. In regard to this difference, it must, however, be noted that the conditions obtaining in the two series of experiments were not quite the same, for in the electrolytic chlorination, hydrogen was continuously evolved from one of the electrodes in the hydrochloric acid solution. It seems probable that the benzyl chloride, which must dissolve to a certain extent in the aqueous solution, is reduced by the nascent hydrogen, and this will result in a smaller proportion of benzyl chloride in the final product.

Series VIII, in which chlorination was effected by electrolytic chlorine in the light, must similarly be compared with series II. The mean values for the proportion of benzyl chloride are approximately the same, and it follows that the action of electrolytic chlorine is not sensibly different from that of ordinary chlorine.

Reference may here be made to the difference in the results which have now been obtained as compared with those communicated in the preliminary note (*loc. cit.*). In the earlier series of experiments, the conditions obtaining in the processes of electrolytic and ordinary chlorination were not sufficiently defined. The electrolytic experiments were made in a badly lighted room, whereas the ordinary chlorinations were effected in good daylight. This is largely responsible for the much greater differences which were found previously for the action of electrolytic chlorine on the one hand, and ordinary chlorine on the other. In the second place, the method previously employed in the analysis of the product of chlorination has been found to be unsatisfactory. This method involved the removal of unchanged toluene by distillation and the oxidation of the residue by means of potassium permanganate. As indicated at the time, the oxidation of the chloro-substitution product by this method is very incomplete, and in the light of later results it appears that the readiness with which the different isomerides undergo oxidation is dependent on their relative proportions in the mixture examined.

The marked influence of moisture on the side-chain nuclear ratio is not peculiar to the chlorination process, for similar effects have been observed in experiments which we have made on the bromination of dry and moist toluene. The bromine used was allowed to remain for some days in contact with potassium bromide, then dried over fused calcium bromide, and distilled over barium oxide. The toluene was freshly distilled over sodium. Fifteen c.c. of a toluene solution, containing 7·2 per cent. by weight of bromine, were introduced into two blackened glass tubes, and 9 milligrams of water were then added to one of the tubes. The preparation of the bromine solution and the filling and sealing of the tubes were effected in a dark room by the aid of a feebly luminous gas flame. The sealed tubes were then placed in a closed box, immersed in a water-bath at 25°, until the bromine had completely disappeared. This occurred in the moist solution after fourteen days, and in the dry solution after thirty days. In a second experiment with a toluene solution containing 8·9 per cent. of bromine, to which in one case 39 milligrams of water were added, fourteen days elapsed before the disappearance of the bromine in the case of the moist solution, the corresponding period for the dry solution being about thirty-five days. The following table gives the relative amounts of side-chain and nuclear substitution products in these experiments:

TABLE III.

		Percentage of	
		Benzyl bromide.	Bromotoluenes.
Experiment 1	Dry solution.........	27·8	72·2
	Moist ,, ...	18·7	81·3
Experiment 2	Dry solution.........	22·5	77·5
	Moist ,, ...	14·2	85·8

According to these data, the presence of water in the toluene reduces the proportion of benzyl bromide, and at the same time increases the rate at which the bromine disappears. The effect is therefore of the same kind as that observed in the chlorination experiments. On account of the wide differences in the conditions of the chlorination and bromination experiments, it is not, however, possible to make any quantitative comparison of the two series of data.

From a consideration of all the observations relating to the chlorination of toluene, it appears to be established that side-chain substitution is favoured by light, rise of temperature,* and absence of moisture. In so far as these factors are concerned, the chlorination of toluene is influenced in the same way as the bromination process. The two processes would also appear to be similarly influenced by the nature of the medium, for when toluene, mixed with its own volume of nitrobenzene, was chlorinated, an increase in the relative proportion of the nuclear substitution product was observed. No data are available to show the influence of the concentration of the halogen in the case of the chlorination process, and on account of the limited solubility of chlorine in toluene at temperatures at which the reaction takes place, it is doubtful whether the influence of concentration could be experimentally determined with any accuracy.

Independently of the influence of the concentration of the halogen, it is clear that the degree of parallelism between the chlorination and bromination processes is such as to warrant the conclusion that the mechanism of the processes is of the same kind. The more extensive observations relating to the bromination of toluene may therefore be utilised in the elaboration of a general theory of halogenation.

Two theories relating to the special case of bromination have already been referred to in this paper. Both of these offer a plausible explanation of certain facts, but, on the whole, the view that nuclear substitution is due to halogen in the form of polyhalogen compounds appears to be the more acceptable. The diminution in the relative amount of nuclear substitution with rise of temperature and with diminishing concentration of the halogen is consistent with the polyhalogen theory, for both these factors are favourable to the dissociation of the polyhalides. The observed increase in the percentage of nuclear substitution product when certain solvents, such as nitrobenzene, benzonitrile, and acetic acid, are added to the toluene is in accord with the fact that these solvents facilitate the formation of polyhalogen compounds. Observations relating to polyiodides indicate that although these are formed to a small extent in hydrocarbons, carbon tetrachloride, chloroform, and carbon disulphide, they are produced in very much larger quantities in nitrobenzene, ethyl acetate, benzonitrile, acetic acid, and certain other solvents. It is this particular property which appears to determine the nuclear substituting influence of these media.

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* The influence of temperature on the nature of the product of chlorination is shown by experiments which were made with carefully dried materials at 0°. The relative amount of chlorine entering the side-chain was found to be 30 per cent. when chlorination took place in the dark and 45 per cent. when the experiment was conducted in the light. The corresponding numbers, obtained when the toluene was heated at its boiling point, are 90 and 94 per cent. respectively. These results show clearly enough the considerable influence of temperature both in the dark and in the light.

That similar relationships hold in respect of the formation of polybromides is rendered probable by the results of distribution experiments which were made with carbon tetrachloride and nitrobenzene. According to Bruner and Dluska (*loc. cit.*), the addition of carbon tetrachloride to toluene produces no alteration in the distribution of the bromine between the side-chain and the nucleus; it acts simply as a diluent, and as such reduces the velocity of the reaction.

Fifty c.c. of *N*-aqueous hydrobromic acid were shaken at 18° with 70 c.c. of carbon tetrachloride and of nitrobenzene respectively. After the liquids had been kept for an hour to allow of complete separation, 50 c.c. of the non-aqueous layer were titrated with 0·1*N*-sodium hydroxide. Less than 0·1 c.c. of alkali was required for neutralisation in the case of carbon tetrachloride, and less than 0·25 c.c. in that of nitrobenzene.

The same experiments were then made after the addition of bromine to the hydrobromic acid solution. The amount of bromine added was such that the composition of the resulting solution could be represented by 1·0*N* ($HBr_{1\cdot5}$). After shaking with this solution, 50 c.c. of each of the non-aqueous liquids were treated with potassium iodide and excess of sodium thiosulphate to remove bromine, and then titrated as before with 0·1*N*-alkali. The carbon tetrachloride required, as previously, less than 0·1 c.c. of alkali, whereas the nitrobenzene required 4·4 c.c., which is approximately twenty times * as much as was required in the absence of bromine. These results show clearly the great difference between the two solvents in regard to the formation of polyhalogen hydrogen compounds.

It is possible that the relative stability of polyhalogen compounds in nitrobenzene solution is connected with the ionising power of this solvent, for the solutions of the polyiodides in nitrobenzene have been shown (Dawson and Gawler, Trans., 1902, **81**, 525; Dawson and Jackson, Trans., 1908, **93**, 2063) to be good conductors. Other solvents, like ethyl acetate and benzonitrile, which favour the formation of polyhalogen compounds and increase the relative amount of nuclear product in the bromination of toluene, also yield solutions which have a high electrical conductivity. Although there is no direct evidence to show that the nuclear substituting effect is conditioned by the ionisation, these facts would seem to indicate that halogen in the form of polyhalogen ion is specially active in this respect.

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* The correct value of the acid ratio is probably very much greater than this, for a large proportion of the 0·25 c.c. of alkali required for titration in the absence of bromine, is due to the acid character of the nitrobenzene.

The fact that solutions of bromine and iodine in moist nitrobenzene are conductors of electricity (Bruner, *Bull. Acad. Sci. Cracow*, 1907, 731) is, at first sight, favourable to the view that nuclear substitution is due to free halogen ions. On the other hand, solutions of chlorine do not conduct (Bruner and Galecki, *Zeitsch. Elektrochem.*, 1910, **16**, 204), and yet the processes of chlorination and bromination appear to be affected in a similar manner when the conditions of the two processes are similarly altered. These facts are difficult to reconcile with the ionic theory of nuclear substitution, and on this account we are inclined to adopt the polyhalogen theory.

Neither this nor the ionic theory appears to offer an immediate explanation of the fact that the presence of water in the toluene increases the relative proportion of the nuclear substitution products. Comparative measurements of the rate of leakage of electricity through dry and moist solutions of chlorine and hydrogen chloride in toluene were made in this connexion, but the results indicate that if there is any difference in the conductivity of the moist and dry solutions, it is not sufficiently large to account for the observed influence of moisture on the chlorination process on the assumption that nuclear substitution is due to chlorine ions. In so far as the resultant effects are concerned, the action of moisture is opposed to that of light, for this increases the rate of side-chain substitution, and the former accelerates the process of nuclear substitution. Before these catalytic effects can be explained, further experiments are necessary.

The question of carriers may finally be discussed. The assumption that the activity of these substances is due to an increase in the concentration of halogen ions as a consequence of the formation of more highly ionised "carrier-halogen" compounds is not, so far as we are aware, supported by any experimental evidence. On the other hand, if such "carrier-halogen" compounds are themselves of the nature of perhalogen compounds, or if they are capable of combining with further quantities of halogen to form such perhalogen derivatives, the formation of nuclear substitution products in the presence of carriers is explicable in terms of the polyhalogen theory without the necessity of formulating any additional electrolytic hypothesis. From a consideration of the valency relationships of the various substances which serve as carriers, it seems likely that all these substances are capable of forming dissociating halogen addition compounds which belong to the polyhalogen type.

In the course of the above experiments, we have observed certain colour phenomena in connexion with the process of chlorination, which we propose to reserve for a further communication. When moist chlorine is passed into boiling toluene in the light, the toluene gradually assumes the yellow colour of chlorine. If, however, hydrogen chloride is passed in simultaneously, the yellow colour disappears, reappearing when the hydrogen chloride is cut off. In the dark the liquid retains its yellow colour in presence of hydrogen chloride. In some cases the chlorination product, after carefully washing free from chlorine and hydrogen chloride, retains a permanent pale yellow colour. The exact conditions which are necessary for the production of the colour change, which is probably due to the formation of a small quantity of a yellow-coloured substance, have not yet been determined.

THE UNIVERSITY,
LEEDS.

CLIII.—*The By-Products of Alcoholic Fermentation.*

By OLIVE EVELINE ASHDOWN and JOHN THEODORE HEWITT.

THE formation of small quantities of carbon compounds other than carbon dioxide and alcohol during the fermentation of various sugars by yeast has attracted much attention, and during the past few years considerable light has been thrown on the formation of some of these by-products. Whilst many endeavours have been made to solve the problem as to why and how succinic acid and the higher alcohols seem to be almost invariable constituents of crude alcohol, comparatively little attention has been devoted to the acetaldehyde which accompanies the alcohol in varying quantity, and which sometimes is formed in considerable amount.

If, however, one desires to throw light on the mechanism of the reaction by which alcohol is produced from dextrose and similar sugars, it is fairly evident that this substance is worthy of much greater attention, since whilst yeast normally produces alcohol with extremely small amounts of acetaldehyde, the fact that the latter substance is occasionally formed in much greater amount during abnormal fermentations is likely to lead to information of value if only the nature of the abnormality is understood.

The occurrence of notable amounts of aldehyde might be referred to one of several possible causes:

1. Subsequent oxidation of alcohol by atmospheric oxygen. This hypothesis necessitates the presence of a catalytic agent, which might either be derived from an inanimate source, for example, some metallic salt the presence of which had been overlooked, or might be of an enzymatic nature and be derived from the yeast or some other organism.

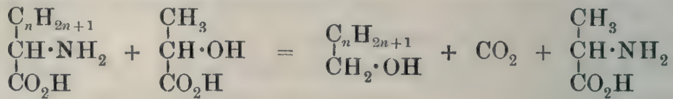
2. The acetaldehyde may be produced from the sugar by a fermentation due to some other organism.

3. Sugars when fermented by yeast normally give ethyl alcohol and carbon dioxide, but owing to malnutrition of the yeast or some similar cause, acetaldehyde may make its appearance in place of ethyl alcohol to a greater or less extent.

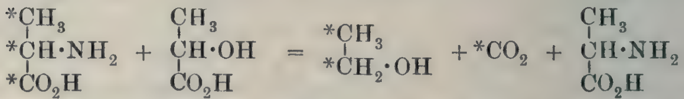
The first or second of these hypotheses may at first sight appear more probable, and one of the present authors at one time inclined to the view that the occurrence of larger amounts of aldehyde than usual was due to some agency outside the yeast. But, as will be seen later, the same yeast will give very varying amounts of acetaldehyde, according to the materials on which it is nourished being altered, other conditions remaining the same, so that the idea of the aldehyde being due to some other agency is out of the question. Moreover, the results obtained by the present authors with yeasts from different breweries show the same result, the production of aldehyde varying at different times with yeast from the same brewery, whilst any possibility of the aldehyde having been produced by subsequent catalytic oxidation owing to the presence of small amounts of salts of heavy metals was carefully excluded by performing all fermenting and distilling operations in glass vessels.

Evidently, then, the aldehyde must be a product derived from the sugar under the action of the yeast, the cause of the variation in amount being due to the different food the yeast is supplied with during fermentation. In order to obtain an idea as to which of the other constituents of the mash could affect the greater or lesser production of aldehyde, systematic experiments were carried out, solutions being made up of known composition. Generally, crystallised sucrose or dextrose was employed, together with necessary mineral constituents, nitrogen being also supplied either in the form of ammonium salts or as amino-acids. In view of the work of F. Ehrlich (*Zeitsch. Ver. deut. Zuckerind.*, 1905, **55**, 539; *Biochem. Zeitsch.*, 1906, **1**, 8; **2**, 52; *Ber.*, 1907, **40**, 1027, etc.) on the production of higher alcohols from the amino-acids with extra carbon atoms (for example, of ordinary *iso*amyl alcohol from leucine), complications were avoided by using alanine as amino-acid, since this can give no other alcohol but ethyl alcohol. In fact, the present authors started the work quite expecting to find that deficiency in available nitrogen would mean increase in aldehyde content, and it was thought not at all unlikely that the function of amino-acids and their conversion into alcohols during fermentation might be connected with the formation of ethyl alcohol and carbon dioxide from some intermediate product, possibly lactic acid.

Assuming that lactic acid is formed as an intermediate product during the alcoholic fermentation of sugars, one might imagine the chemical change involved to be capable of representation in the following (or similar) manner:

I. 

$$\begin{array}{c}C_nH_{2n+1}\\ \vert\\ CH\cdot NH_2\\ \vert\\ CO_2H\end{array} + \begin{array}{c}CH_3\\ \vert\\ CH\cdot OH\\ \vert\\ CO_2H\end{array} = \begin{array}{c}C_nH_{2n+1}\\ \vert\\ CH_2\cdot OH\end{array} + CO_2 + \begin{array}{c}CH_3\\ \vert\\ CH\cdot NH_2\\ \vert\\ CO_2H\end{array}$$

II. 

$$\begin{array}{c}{}^{*}CH_3\\ \vert\\ {}^{*}CH\cdot NH_2\\ \vert\\ {}^{*}CO_2H\end{array} + \begin{array}{c}CH_3\\ \vert\\ CH\cdot OH\\ \vert\\ CO_2H\end{array} = \begin{array}{c}{}^{*}CH_3\\ \vert\\ {}^{*}CH_2\cdot OH\end{array} + {}^{*}CO_2 + \begin{array}{c}CH_3\\ \vert\\ CH\cdot NH_2\\ \vert\\ CO_2H\end{array}$$

That a plentiful supply of nitrogen in the form of ammonium salts or as alanine would reduce the amount of aldehyde to any appreciable extent was immediately negatived by the results obtained with a series of fermentations carried out on sucrose solutions to each of which equal amounts of potassium phosphate, magnesium sulphate, and calcium phosphate had been added, but which differed respectively in containing (*a*) no added nitrogenous material, (*b*) ammonium sulphate, (*c*) ammonium tartrate, and (*d*) alanine. A reference to table II, which records the results obtained with a Yorkshire yeast at the ordinary temperature (Jan., 1909) over a period of nineteen days, shows that whilst the largest yield of alcohol was obtained when alanine was added, and the next best yield with ammonium sulphate, least aldehyde was formed when the yeast had to depend on its own nitrogen, and the greatest amount (absolutely—the amount relatively to the alcohol formed was slightly greater in the case of ammonium tartrate) was produced when alanine was added. Evidently lack of nitrogenous food is not the cause of aldehyde formation, and a systematic search for ferments, whether inorganic or enzymic, which can effect a catalytic decomposition of alanine with production of acetaldehyde would seem desirable in view of the observation made by E. Drechsel (*Ber.*, 1892, **25**, 3502), that alanine heated alone, or, still better, with an excess of concentrated phosphoric acid, to 220—230°, is decomposed into acetaldehyde, carbon monoxide, and ammonia, according to the equation:

$$CH_3\cdot CH(NH_2)\cdot CO_2H = CH_3\cdot CHO + CO + NH_3.$$

Drechsel draws particular attention to the wandering of an oxygen atom of the carboxyl group (presumably the hydroxylic oxygen) to the *a*-carbon atom, and it seems not unreasonable to suppose that, given a suitable enzyme, a similar transformation, resulting in the formation of acetaldehyde and formamide or ammonium formate, might be effected at the ordinary temperature.

During the progress of this work we fortunately turned our attention to a paper by H. Schade (*Zeitsch. physikal. Chem.*, 1906, **57**, 1), who had discovered a method of fermenting dextrose to ethyl alcohol and carbon dioxide without the aid of any organism or organic enzyme. Briefly, this author found that dextrose is decomposed by alkalis with the formation of acetaldehyde and a formate, whilst acetaldehyde and formic acid yield ethyl alcohol and carbon dioxide under the influence of rhodium sponge. Schade thinks it not improbable that yeast effects the conversion of dextrose into ethyl alcohol and carbon dioxide in a somewhat similar manner, dextrose decomposing into an intermediate product, which in turn yields formic acid and acetaldehyde, an enzyme functioning in a similar manner to rhodium sponge then coming into play.

The nature of the intermediate compound which furnishes the acetaldehyde and formic acid (if the hypothesis of Schade is correct) is not quite clear; presumably the dextrose must first decompose to yield two molecular proportions of a compound, $C_3H_6O_3$, and perhaps the simplest assumption would be to regard this compound as lactic acid (compare Buchner and Meisenheimer, *Ber.*, 1904, **37**, 417; 1905, **38**, 620), which may furnish either ethyl alcohol and carbon dioxide directly, or else give acetaldehyde and formic acid, which may in turn react to give the end-products mentioned. It should, however, be noticed that a comparatively recent paper by P. Boysen Jensen (*Ber. Deut. bot. Ges.*, 1908, **26**, *A*, 666) assumes that dihydroxyacetone is an intermediate product in the fermentation of dextrose to ethyl alcohol and carbon dioxide, for the oxime of this ketone is stated to have been isolated when hydroxylamine was added to a fermenting dextrose solution. Jensen consequently divides the fermentation of dextrose into stages:

$$C_6H_{12}O_6 \longrightarrow 2OH\cdot CH_2\cdot CO\cdot CH_2\cdot OH \longrightarrow 3CH_3\cdot CH_2\cdot OH + 2CO_2.$$

and supposes that zymase consists of two enzymes, the first capable of effecting the conversion of dextrose into dihydroxyacetone, the second decomposing the latter into ethyl alcohol and carbon dioxide. He further states that an addition of glycerol inhibits the second reaction, so that in these circumstances dihydroxyacetone is isolated as the final product. This ketone may be decomposed by an oxydase, but in this case carbon dioxide and water are produced, no alcohol being formed.

Quite recently E. Buchner and J. Meisenheimer (*Ber.*, 1910, **43**, 1773) have published the results of exhaustive experiments on the action of yeast, both living and as yeast juice, on a number of compounds containing a chain of these carbon atoms; their results are interpreted as disposing of the possible fermentation of lactic acid, methylglyoxal, or glyceraldehyde to ethyl alcohol and carbon dioxide, although with dihydroxyacetone and yeast juice, boiled yeast juice having been added (see A. Harden and W. Young, Proc., 1905, **21**, 189; E. Buchner and H. Haehn, *Biochem. Zeitsch.*, 1909, **19**, 192), no less than 80 to 90 per cent. was fermented to alcohol and carbon dioxide. This result is even more striking than that of G. Bertrand (*Ann. Chim. Phys.*, 1904, [viii], **3**, 257), who succeeded in fermenting 25 per cent. of this triose.

There seems to be a consensus of opinion that some intermediate product, probably of the formula $C_3H_6O_3$, is produced, and that this gives rise to alcohol and carbon dioxide either directly or possibly with the intermediate formation of acetaldehyde and formic acid, although Buchner and Meisenheimer consider Schade's view quite untenable (*Ber.*, 1906, **39**, 4218; 1910, **43**, 1782).

This objection is based on the negative results obtained in attempting to ferment a mixture of acetaldehyde and formic acid; of course, the harmful influence of these materials might be the cause of the enzyme being put out of action, but later experiments, in which yeast juice has been allowed to act on ethylidene oxide diacetate, $[CH_3\cdot CH(O\cdot CHO)]_2O$, in which the aldehyde and formic acid are only produced slowly by a gradual hydrolysis, have proved no more successful.

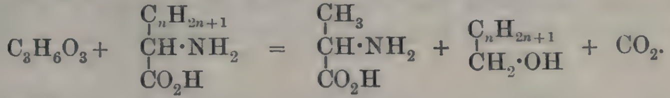
From these experiments of Buchner and Meisenheimer, it would appear that any possibility of formic acid playing a part in fermentation was out of the question, but, as our experiments show, the amount of acetaldehyde formed is largely reduced when a formate is present, whilst the use of small quantities of formic acid as an aid to good fermentations has been strongly advocated by H. Lange (*Zeitsch. f. Spiritusind*, 1905, **28**, 341).

It seems to us not improbable that some substance, possibly alanine, which should ferment normally to give ethyl alcohol and carbon dioxide, may be formed either as a product of the decomposition of the dextrose or perhaps as a transformation product of dihydroxyacetone in presence of nitrogenous material. Such a substance can give rise to acetaldehyde (Drechsel, *loc. cit.*); it may be that in presence of formic acid this latter reaction takes place to a more limited extent; certainly the fact remains that the presence of formates strongly diminishes the amount of acetaldehyde produced in alcoholic fermentation.

Without in any way committing ourselves to an explanation of the mechanism of the process, we think the following scheme may perhaps represent the course followed during the fermentation of dextrose to ethyl alcohol and carbon dioxide:

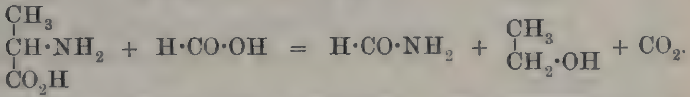
I. $C_6H_{12}O_6 \longrightarrow 2C_3H_6O_3$ ($?\,HO\cdot CH_2\cdot CO\cdot CH_2\cdot OH$).

II.



$$C_3H_6O_3 + \begin{array}{c}C_nH_{2n+1}\\|\\CH\cdot NH_2\\|\\CO_2H\end{array} = \begin{array}{c}CH_3\\|\\CH\cdot NH_2\\|\\CO_2H\end{array} + \begin{array}{c}C_nH_{2n+1}\\|\\CH_2\cdot OH\end{array} + CO_2.$$

III.



$$\begin{array}{c}CH_3\\|\\CH\cdot NH_2\\|\\CO_2H\end{array} + H\cdot CO\cdot OH = H\cdot CO\cdot NH_2 + \begin{array}{c}CH_3\\|\\CH_2\cdot OH\end{array} + CO_2.$$

IV. $C_3H_6O_3 + H\cdot CO\cdot NH_2 = H\cdot CO_2H + CH_3\cdot CH(NH_2)\cdot CO_2H$.

This represents small quantities of formic acid or formamide acting together with an enzyme of the yeast as catalytic agent; the occurrence of small amounts of one or other of these substances being quite possible in the light of Drechsel's work. In fact, the migration of oxygen from the carboxyl group to the *a*-carbon atom in Drechsel's reaction can best be explained by the assumption of the following intermediate actions:

I. $CH_3\cdot CH(NH_2)\cdot CO_2H = CH_3\cdot CH{:}NH + H\cdot CO_2H$ (or $CO + H_2O$).
II. $CH_3\cdot CH{:}NH + H\cdot CO_2H = CH_3\cdot CH{:}O + H\cdot CO\cdot NH_2$.
III. $H\cdot CO\cdot NH_2 = NH_3 + CO$.

The first of these reactions will be observed to be fully analogous to the well-known decomposition of an *a*-hydroxycarboxylic acid into an aldehyde and formic acid or its decomposition products. With reference to the possibility of formic acid playing a part in alcoholic fermentation, attention may be drawn to F. Ehrlich's views on the decomposition of leucine and the occurrence of valeraldehyde as a by-product (*Ber.*, 1907, **40**, 1046).

The view now advanced, that dextrose decomposes into half-molecules (? dihydroxyacetone), and that these in turn furnish alanine under the action of small amounts of formamide, the alanine then reacting with formic acid under the influence of an enzyme to give ethyl alcohol and carbon dioxide with the regeneration of formamide, would gain much in probability if direct synthesis of *a*-amino-acids from aldehydes and formamide were known; despite a careful search of chemical literature, we have found no synthesis of such a kind, and we are unfortunately prevented at the present time from carrying out a research in this direction. We may, however, sum up the arguments in favour of the suggested hypothesis.

1. The production of ethyl alcohol from alanine during fermentation by yeast brings the formation of the former substance

into line with that of its higher homologues from the higher amino-acids.

2. Acetaldehyde is always formed during the fermentation of dextrose by yeast; our experiments show that the quantity is in no way diminished by an increased supply of nitrogen, whilst Drechsel has shown that alanine yields acetaldehyde and the decomposition products of formamide (carbon monoxide and ammonia) on heating.

3. If alanine is an intermediate product of the conversion of dextrose into ethyl alcohol and carbon dioxide, the formation of lactic acid, which Slator * regards as a by-product, is easily accounted for.

4. The hypothesis that formic acid and formamide play a part in the production of ethyl alcohol receives support from Schade's observation of the reaction between aldehyde and formic acid with rhodium as catalytic agent, and our experiments clearly show that with small quantities of formates initially present, the amount of acetaldehyde formed during fermentation is very markedly decreased.

We may incidentally draw attention to the greater amount of higher alcohols produced when no ammonium salts or alanine were added to the sugar solutions; seeing that in this case the yeast must draw on its own store of nitrogen with concomitant degradation of different amino-acids (leucine, etc., not merely alanine), one has a striking, if somewhat unnecessary, confirmation of Ehrlich's views as to the formation of the higher alcohols.

EXPERIMENTAL.

The yeasts employed in these experiments were not pure cultures, but of known origin, and the authors desire to express their warm thanks to Messrs. J. L. Baker, A. R. Ling, and J. H. Millar for their kindness in supplying them with the necessary material. The usual procedure was to mix 5 grams of the pressed yeast with 10 c.c. of water, and add the resulting cream to a solution of 100 grams of sugar in 1 litre of water.

The use of solutions made up artificially with either sucrose or dextrose, potassium phosphate, magnesium sulphate, and calcium phosphate, and when nitrogenous material was also added, either alanine or ammonium sulphate or tartrate, was preferred to the employment of beer wort, as a complete check on the material

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* Lactic acid seems to be out of the question as the intermediate product between dextrose and ethyl alcohol and carbon dioxide. See A. Slator, Trans., 1906, **89**, 141; 1908, **93**, 231; *Ber.*, 1907, **40**, 123; and E. Buchner and J. Meisenheimer, *Ber.*, 1910, **43**, 1776, 1785.

supplied to the yeast was thus obtained. The solutions were made with boiling water, and subsequently aerated, but any access of air during the fermentation was excluded, owing to the necessity of connecting the Winchester-quart bottles in which the operation was conducted with washing tubes, so that all the escaping carbon dioxide passed through about 50 c.c. water to retain any aldehyde or other vapour carried off by the stream of gas. It is probable that the lack of aeration explains the somewhat small yield of alcohol obtained in many cases. In some experiments fermentation was allowed to proceed at the prevailing temperature, in others the temperature was maintained at 30°. In the latter case all the Winchester-quart bottles of one set of experiments were immersed in the same water-bath, so that temperature conditions should be strictly comparable.

At the end of a fermentation experiment, the contents of the bottle and the attached washing-tube were transferred to a flask and distilled with the aid of a rod-and-disk stillhead furnished with a thermometer; the distillation was always allowed to proceed several minutes after the temperature-reading had shown that water alone was passing over, thus ensuring that all volatile by-products were carried over in the current of steam. A second distillation was usually resorted to in order to concentrate the alcohol sufficiently for the necessary estimations. It is scarcely necessary to remark that considerable pains were exercised in cooling the vapours; the end of the condenser passed into a flask through a cork, which also carried a long reflux tube, so as to ensure volatile constituents being retained.

Besides estimating alcohol in the distillates, the amounts of volatile acid, esters, aldehyde, and higher alcohols were also determined; furfuraldehyde proved to be absent or present only in indeterminable traces. The estimations of the secondary constituents were carried out essentially according to the methods recommended by Girard and Cuniasse (*Manuel pratique de l'Analyse des Alcools et des Spiritueux*, Paris, 1899), and since comparative results were chiefly desired, the colorimetric method for estimating the higher alcohols, using an *iso*butyl alcohol standard, was adopted. Both in this case and in estimating the acetaldehyde colorimetrically, several standard solutions were always employed, and the colour developed was matched against the nearest standard. In this way much of the uncertainty experienced in using two liquids of very different intensity of colour was avoided.

The lack of any very close connexion between the supply of nitrogen and the amount of aldehyde produced is shown by the set of experiments recorded in table I.

TABLE I.

Five grams of Yorkshire yeast, stirred up with 10 c.c. of water, were added to each of five solutions. Each of these five solutions contained 200 grams of sucrose, 10 grams of potassium phosphate, 10 grams of magnesium sulphate, and 1·0 gram of calcium phosphate (for added nitrogenous material see the table itself). The yeast was added on Jan. 6th, 1909, the temperature maintained at 30° for sixty-six hours, and, after a further sixty-five hours at 10—15°, the fermented liquids were distilled on Jan. 11th.

None of the results are good as regards alcohol production; the temperature employed was unsuitable for the yeast in question; the highest yield of alcohol was, however, obtained when nitrogenous material was added in the form of alanine. The much greater production of higher alcohols where the yeast had merely its own nitrogen to depend on (experiment 2) is very noticeable.

Experiment …………	1.	2.	3.	4.	5.
Added nitrogenous material.	16 grams ammonium sulphate.	None.	20 grams alanine.	30 grams ammonium tartrate.	20 grams ammonium tartrate.
Yield of alcohol (in grams)	66·2	35·4	67·5	33·5	42·8
By-products; expressed as grams per 100 litres of absolute alcohol.					
Acids ………………………	—	27·1	30·3	53·8	41·4
Esters ………………………	—	45·7	19·4	55·2	73·5
Aldehydes …………………	71·3	52·5	53·2	81·3	66·1
Higher alcohols……………	120·0	255·2	141·0	44·4	80·0

TABLE II.

In another set of experiments, using exactly the same materials and some of the same sample of yeast, but where the fermentation was allowed to proceed at the ordinary temperature for nineteen days (Jan. 6th to 25th, 1909), much better yields of alcohol were obtained.

Experiment …………	1.	2.	3.	4.	5.
Added nitrogenous material.	16 grams ammonium sulphate.	None.	20 grams alanine.	30 grams ammonium tartrate.	20 grams ammonium tartrate.
Yield of alcohol (in grams)	80·7	41·2	84·75	52·4	56·0
By-products; expressed as grams per 100 litres of absolute alcohol.					
Acids ………………………	40·6	29·1	23·3	45·4	30·5
Esters ………………………	67·3	34·1	63·3	76·0	67·0
Aldehydes …………………	28·2	6·9	84·3	86·0	91·3
Higher alcohols……………	34·2	38·2	—	14·7	46·0

The amounts of alcohol produced under these more favourable conditions as to temperature are considerably larger; the small amount obtained in experiment 2 is only to be expected, the yeast being starved with regard to nitrogen. The particular experiment is instructive, so small an amount of aldehyde having been produced, a result with which we were much surprised at the time, as we thought the increased production of aldehyde probably depended on the yeast obtaining insufficient nitrogenous food. It is also interesting that the absolutely largest quantity of aldehyde was produced when alanine was supplied.

TABLE III.

In order to control the foregoing results, experiments were made using dextrose solutions and fermenting with a London beer yeast at 30°. Each solution contained 100 grams of dextrose (crystallised, colourless), 5 grams of potassium phosphate, 5 grams of crystallised magnesium sulphate, and 0·5 gram of calcium phosphate in 1 litre of water. To each solution 5 grams of yeast, stirred up with 10 c.c. of water, were added on Jan. 28th, 1909, and the solutions were distilled on Feb. 2nd.

Experiment	1.	2.	3.
Added nitrogenous material	8·0 grams ammonium sulphate.	None.	10·0 grams ammonium tartrate.
Alcohol produced (in grams)...............	37·8	31·8	40·9
Grams of aldehyde per 100 litres alcohol	50·0	13·1	51·8

Again the small yield of alcohol where no nitrogenous material was added is noticeable, and, as before, least aldehyde was also formed. The yeast from experiment 2 was therefore used to ferment a fresh dextrose (100 grams) solution (in 1 litre of water), salts being added as before, and also 10 grams of ammonium tartrate. 39·4 Grams of absolute alcohol were then obtained, and the aldehyde figure had risen to 41·0. In this experiment fermentation proceeded for ninety hours at 30°.

Thus there can be no doubt that a plentiful supply of nitrogen, instead of diminishing the aldehyde, rather tends to increase the amount produced. We, consequently, in the light of Schade's work, turned our attention to the influence of formates on the production of aldehyde, and found that the quantity was considerably reduced; instead of 30 to 90 parts of aldehyde per 100,000 of absolute alcohol, numbers from 5 to 20 (sometimes more) were usually obtained. The amounts of sodium formate employed were much larger than necessary in our earlier experiments (1 to 9 in table IV), so that occasionally slightly more aldehyde was produced when 10 instead of 5 grams of sodium formate were employed to 100 grams of sucrose, the excess material being probably without much influence.

TABLE IV.

In the following four sets of experiments, in each separate experiment a solution was made up with 100 grams of sucrose, 5 grams of potassium phosphate, 5 grams of magnesium sulphate, and 0·5 gram of calcium phosphate to 1 litre of boiling water. The amount and form in which nitrogen was added or not is shown in the table. After cooling, the solutions were aerated, and 5 grams of yeast stirred up with 10 c.c. water added in each case.

In experiments 1 to 5 a beer yeast was added on March 13th, 1909, and a temperature of 30° was maintained for about ninety hours (see table). Experiments 6 to 9 were started on the same day with some of the same yeast, but fermentation was allowed to proceed at the prevailing laboratory temperature until March 25th.

In experiments 10 to 17 a porter yeast was added on May 5th, 1909, the temperature was kept at 30° for three days, and fermentation stopped after a further two days at the laboratory temperature.

A beer yeast was again employed for experiments 18 to 25, the fermentation was started on June 3rd, 1909, the temperature maintained for two days at 30°, and the fermentation stopped after a further two days at the laboratory temperature.

The results recorded in the following table demonstrate the far larger amounts of aldehyde usually produced when formates are absent, and evidently comparing the first nine experiments with the succeeding ones, quantities of sodium formate ranging from 5 to 10 per cent. of the weight of the sucrose are quite unnecessary. Turning to the strictly comparable set of experiments 10 to 13, the increasing amount of aldehyde with the decreasing amount of sodium formate is very noticeable; in another strictly comparable set, namely, 22 to 25, exactly the same phenomenon is noticed. In set 14 to 17, slight irregularities are observed, but here in each case the aldehyde-content was fairly low, and the same remark applies to experiments 18 to 21, in which, compared with the other three experiments, No. 18 has given a somewhat anomalous result.

The record of the determinations of volatile acids (calculated as acetic acid) and esters (as ethyl acetate) has been given, but although care was taken to obtain all the alcohol and by-products produced, no attempt was made to get all the distillates of the same alcoholic strength, or time given to allow the equilibrium:

$$\text{alcohol} \times \text{acid} / \text{ester} \times \text{water} = \text{a constant}$$

to be attained, so that varying ratios of acids to esters are not to be wondered at.

			Other materials added to solution (grams).				By-products ; grams per 100 litres absolute alcohol.			
Expt.	Duration of fermentation.	Temperature.	Sodium formate.	Ammonium sulphate.	Ammonium tartrate.	Alcohol produced (grams)	Acids.	Esters.	Aldehyde.	Higher alcohols.
1	88 hours	30°	5	8	—	41·4	37·4	67·5	16·7	75·8
2	90½ ,,	30	10	8	—	45·6	22·4	77·9	22·0	139·0
3	91½ ,,	30	5	—	—	45·3	20·8	61·0	50·0	90·9
4	92¼ ,,	30	10	—	—	45·1	12·4	67·5	3·8	33·65
5	95½ ,,	30	10	—	10	47·5	12·7	99·5	20·5	64·8
6	12 days	15	5	8	—	45·6	22 8	58 1	40 6	71·4
7	12 ,,	15	10	8	—	47·6	14·5	91·0	33·0	70·9
8	12 ,,	15	5	—	—	36·2	17 1	100·2	21·9	182·0
9	12 ,,	15	10	—	—	37·3	14·5	113·2	29·0	100·0
10	3 ,, 2 ,,	30 15	2	8	—	43·0	23·3	150 0	11·1	58·8
11	3 ,, 2 ,,	30 15	0·5	8	—	46·0	38 2	88 0	15 6	105·0
12	3 ,, 2 ,,	30 15	0·1	8	—	42·7	67·4	98·3	41·7	160·0
13	3 ,, 2 ,,	30 15	0	8	—	41·2	58·9	88 4	53·2	140·0
14	3 ,, 2 ,,	30 15	2	—	—	43·9	18·9	85·0	24·1	180·0
15	3 ,, 2 ,,	30 15	0·5	—	—	41·9	26 9	73·2	30·0	130·0
16	3 ,, 2 ,,	30 15	0·1	—	—	43·5	11·4	48·4	11·4	129·0
17	3 ,, 2 ,,	30 15	0	—	—	41·0	18·6	46·1	14·75	165·0
18	2 ,, 2 ,,	30 15	2	8	—	37 2	33·5	129·0	24·0	70·8
19	2 ,, 2 ,,	30 15	0·5	8	—	43·3	32·4	190·3	8·8	30·2
20	2 ,, 2 ,,	30 15	0·1	8	—	39·4	60·6	228·6	20·0	95·2
21	2 ,, 2 ,,	30 15	0	8	—	37·0	56·5	162 6	23·7	74·1
22	2 ,, 2 ,,	30 15	2	—	—	33·6	28·7	46·1	24 6	79·4
23	2 ,, 2 ,,	30 15	0·5	—	—	32·5	18·1	122·3	27·4	76·9
24	2 ,, 2 ,,	30 15	0·1	—	—	30·8	14·7	109·1	32 0	99·0
25	2 ,, 2 ,,	30 15	0	—	—	32·5	14·5	—	51·3	191·0

The yields of alcohol, as we have previously mentioned, are far from ideal, but it has to be remembered that after the first aeration following the making up of the solutions, the fermentations were carried on without any access of air, and in some cases there is no doubt that an insufficient supply of nitrogen contributed to lack of vigour on the part of the yeast. This is well seen by comparing experiments 8 and 9 (mean amount of alcohol 36·7 grams) with 6 and 7 (47·1 grams), or experiments 22 to 25 with 18 to 21.

We think, however, our experiments conclusively show that the amount of aldehyde is markedly diminished by the presence of formates during fermentation, and although Schade's original theory as to the rôle played by formic acid in fermentation may need modification, it should not too lightly be set on one side.

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CLIV.—*The Absorption Spectra of Furan, Furfuraldehyde, Thiophen, and Pyrrole under Different Conditions.*

By John Edward Purvis.

In this communication an account is given of a comparative study of the absorption spectra of furan, furfuraldehyde, thiophen, and pyrrole, as vapours at various temperatures and pressures, in solution and as liquids, in order to ascertain the nature and extent of the selective absorption under these various conditions.

The apparatus employed has been already described in previous communications (this vol., pp. 692, 1035). The substances were distilled several times before being used. Not much furan was available, so that only two series of observations of the vapour at increasing temperatures and pressures were possible; and none were taken at decreased pressures. Alcoholic solutions of the substances were, however, examined, in order to compare them with those of furfuraldehyde.

Table I.

Furan.—The absorption bands in furan vapour at various temperatures and pressures in a column 100 mm. long. Barometric pressure = 749 mm.

Abbreviations: w. = weak; v.w. = very weak; str. = strong; narr. = narrow; f.wide = fairly wide; f.w. = fairly weak; mod. str. = moderately strong.

13°. 749 mm.		30°. 793 mm.		45°. 819 mm.	
λ.		λ.		λ.	
2652	w., wide	2652	w., wide	2652	w., wide
2647	,,	2647	,,	2647	,,
2642	,,	2642	,,	2642	,,
2637	f.wide, w.	2637	f.wide, w.	2637	f.wide, w.
2634	,, str.	2634	,, str.	2634	,, str.

13°.
749 mm.

λ.	
2630	narr., w.
2627	f. wide, w.
2620	wide, w.
2601	narr., w.
2599	,,
2593	f. wide, w.
2589	head of strong band, sharp on more refrangible side.
2541	f. wide, w.
2538	,,
2530	head of strong band, sharp on more refrangible side.

The rays were then transmitted to Cd 2265, but they were very weak between 3370 and Cd 2329.

15 bands.

30°.
793 mm.

λ.	
2630	narr., w.
2627	w., f. wide
2620	w., wide
2601	w., narr.
2599	,,
2593	f. wide, w.
2589	head of strong band
2541	w., f. wide
2538	,,
2530	head of strong band

The rays were then transmitted to about 2420, but the series of Cd lines from 2329 to 2265 were well marked.

15 bands.

45°.
819 mm.

λ.	
2630	w., narr.
2627	w., f. wide
2620	w., wide
2601	w., narr.
2599	,,
2593	f. wide, w.
2589	head of strong band
2541	w., f. wide
2538	,,
2530	head of strong band

The rays were then transmitted to about 2470; the Cd lines 2329 to 2265 were well marked.

15 bands.

60°.
849 mm.

λ.	
2652	w.
2647	w.
2642	w.
2637	w.
2634	f. w.
2630	w.
2627	w.
2620	w.
2601	w.
2599	w.
2593	w.
2589	mod. str.
2541 2538 2530	v. w., only just visible

The rays were then transmitted to about 2500; the Cd lines 2329, 2321, 2313, and 2288 were just visible.

15 bands.

75°.
879 mm.

λ.	
2652	v. w.
2647	,,
2642	,,
2637	,,
2634	,,
2630	,,
2627	,,
2620	,,
2601	,,
2599	,,
2593	,,

The rays were then transmitted to about 2560, and general absorption after that.

11 bands.

90°.
909 mm.

No bands were seen; and general absorption from 2700, the strong Cd line 2573 being just visible.

No bands.

The effect of increasing the temperatures and pressures was not to show up any new bands, but the bands noticed at 13° and 749 mm. pressure were slightly wider and stronger at the increased temperatures and pressures. The bands at 2589 and 2530 were very similar in appearance, as were also 2634 and 2627. The three weak bands 2652, 2647, and 2642 were similar, and differ in their wave-lengths by about 5 units. The bands 2541, 2530, and 2599, 2589 form a group differing by equal wave-lengths.

Besides that, the bands can be considered as a whole, and show differences of wave-lengths, for example:

2652			
15	2647		
2637	13	2642	
10	2634	12	mean = 14
2627	14	2630	
28	2620	15	mean = 13
2599	27	2601	
58	2593		
2541	55	2589	
	2538	59	mean = 57 = 13·5 × 5
		2530	

The numbers should be read diagonally, and from left to right.

Table II.

Furfuraldehyde.—The absorption bands in furfuraldehyde vapour at various temperatures and pressures in a column 100 mm. long.

Abbreviations: w. = weak; narr. = narrow; sh. = sharp; f.str. = fairly strong; v.w. = very weak; str. = strong.

17°. 763 mm.	30°. 807 mm.	45°. 833 mm.
λ.	λ.	λ.
2726 w., narr., sh.	2726 w., narr.	2726
2725 narr., sh., stronger than 2726	2725 w., wider than at 17°	2725
2720 w., narr.	2720 ,, ,,	General absorption began at λ 2720.
2718 ,,	2718 ,, ,,	
2712 f.str.	2712 ,, ,,	
2709 stronger than 2712	2709 ,, ,,	2 bands.
2706 w., narr.	General absorption began at λ 2700.	
2704 stronger than 2706		
2701 w., narr.		
2699 ,,		
2697 ,,		60°. 863 mm. λ.
General absorption began at λ 2695; the Cd lines 2329 to 2194 were just visible.		No bands. General absorption began at λ 3730.
11 bands.	6 bands.	No bands.
75°. 893 mm. λ.	90°. 923 mm. λ.	100°. 939 mm. λ.
No bands. General absorption began at λ 2740.	No bands. General absorption began at Cd 2748.	No bands. General absorption began at about Cd 2748.

TABLE III.

The absorption bands in furfuraldehyde in a column 100 mm. long at a constant temperature of 12° and under varying pressures. Abbreviations as in table I.

8 mm.

λ.	
2721	v.w.
2718	,,
2712	,,
2709	,,
2706	,,
2704	,,
2702	,,
2698	w.
2696	stronger than 2698
2688	str.
2681	f.w.
2679	stronger than 2681
2676	w.
2674	stronger than 2676
2668	w.
2666	stronger than 2668
2660	
2654	w.
2652	stronger than 2654
2641	w.
2639	stronger than 2641

General absorption began at λ 2620; the Cd lines 2573, 2329, 2321, 2313, 2288, 2265, 2194, and 2144 were visible.

21 bands.

158 mm.

λ.

The same series of bands were visible as at 8 mm. pressure; the chief difference was that the Cd lines 2573 to 2194 were weaker.

21 bands.

308 mm.

λ.

The same series of bands were visible as at 8 mm. and 158 mm. pressure but the Cd lines from 2573 to 2194 were weaker.

21 bands.

458 mm.

λ.	
2721	v.w.
2718	,,
2712	,,
2709	,,
2706	,,
2704	,,
2702	,,
2698	w.
2696	w.
2688	w.
2681	w.
2679	w.
2676	w.
2674	w.

General absorption at λ 2650; the Cd lines 2573 to 2144 were very weak.

14 bands.

608 mm.

λ.	
2721	v.w.
2718	,,
2712	,,
2709	,,
2706	,,
2704	,,
2702	,,
2698	,,
2696	,,
2688	,,
2681	,,
2679	,,

General absorption from λ 2670; the Cd lines from 2573 to 2144 were very weak.

12 bands.

738 mm.

λ.	
2721	v.w.
2718	,,
2712	,,
2709	,,
2706	,,
2704	,,
2702	,,
2698	,,
2696	,,
2688	,,

General absorption from λ 2680; the Cd line 2573 was just visible, and the Cd lines from 2329 to 2194 were only just visible.

10 bands.

TABLE IV.

The absorption bands of furfuraldehyde in a column 100 mm. long at a constant temperature of 100° and under varying pressures. Abbreviations as in table I.

8 mm.	158 mm.	308 mm.
λ.	λ.	λ.
2676 v.w.	2702 v.w.	2712 v.w.
2674 ,,	2698 ,,	2709 ,,
2668 ,,	2696 ,,	2706 ,,
2666 ,,	2688 ,,	2704 ,,
2593 w., wide	2681 ,,	2702 ,,
2589 ,,	2679 ,,	2698 ,,
2530 ,,	2676 ,,	2696 ,,
	2674 ,,	2688 ,,
The rays were then transmitted to Cd 2194.	2668 ,,	2681 ,,
	2666 ,,	2679 ,,
	2660 ,,	2676 ,,
	2654 ,,	2674 ,,
	2652 ,,	2668 ,,
	2641 ,,	2666 ,,
	2639 ,,	2660 ,,
	2593 ,,	2654 ,,
	2589 ,,	2652 ,,
	2530 ,,	
	General absorption from λ 2420, the Cd lines from 2329 to 2194 being visible.	General absorption from λ 2650, the Cd 2673 and the Cd lines from 2329 to 2144 being visible.
7 bands.	18 bands.	17 bands.

458 mm.	608 mm.	738 mm.
λ.	λ.	λ.
2721 v.w.	2721 v.w.	No bands. General absorption from λ 2720.
2718 ,,	2718 ,,	
2712 ,,	2712 ,,	
2709 ,,	2709 ,,	
2706 ,,	2706 ,,	
2704 ,,	2704 ,,	
2702 ,,	2702 ,,	
2698 ,,		
2696 ,,	General absorption from 2700.	
General absorption from λ 2694; the Cd lines 2329 to 2194 were just visible.		
9 bands.	7 bands.	

The distinguishing features of the vapour of furfuraldehyde were that at the lower pressures the bands were sharper and slightly narrower than at the higher pressures, and that more bands were visible. Also, that the bands occur chiefly in groups of two, the distances of the constituents being about 2 units, and that they became wider and wider as the wave-lengths decrease; for example, λ 2696 was slightly wider and stronger than λ 2698; λ 2679 was wider and stronger than λ 2681. Besides that, if we consider these groups amongst themselves, they become wider as the wave-lengths decrease; for example, the members of the group 2641—2639 were wider than those of 2698—2696, but they were not so strong; and if the bands are considered as a whole, most of them show fairly even differences of wave-lengths, as the following arrangement indicates:

2726			2718				
24	2725		30	2712			
2702	27	2721	2688	31	2709		
34	2698	25	34	2681	30	2706	
2668	32	2696	2654		2679	30	2704
	2666	36	61	2652	38	2676	30
		2660	2593	63	2641	37	2674
				2589		2639	

Thiophen.—Pauer (*Wied. Ann.*, 1897, **61**, 363) found that no bands were observed in the vapour of thiophen in a tube 100 mm. long, and that general absorption began at about λ 2460.

The author has examined the vapour of thiophen in a column 200 mm. long, and has discovered a few bands.

TABLE V.

The absorption bands of thiophen in a column 200 mm. long at various temperatures and pressures. Abbreviations as before.

20°.	30°.	45°.
761 mm.	805 mm.	831 mm.
λ.	λ.	λ.
2590 w., narr. 2530 ,, 2500 w., wide	2590 w., narr. 2530 ,,	2590 w. 2530 w.
General absorption began at λ 2490.	General absorption began at λ 2500.	Both these bands are wider than at 30° and 761 mm. General absorption began at λ 2505.
3 bands.	2 bands.	2 bands.
60°.	70°.	90°.
861 mm.	891 mm.	921 mm.
λ.	λ.	λ.
2590 w. 2530 w.	No bands. General absorption began at λ 2640, Cd 2573 being visible.	No bands. General absorption began at λ 2720.
Both bands are a little wider than at 45° and 831 mm. General absorption began at λ 2520.		
2 bands.	No bands.	No bands.

TABLE VI.

The absorption bands of thiophen vapour in a column 200 mm. long at a constant temperature of 15° and under varying pressures.

14 mm.	164 mm.	314 mm.
λ.	λ.	λ.
No bands. General absorption began at λ 2420.	No bands. General absorption began at λ 2460.	2590 v.w. 2530 ,,
		General absorption at λ 2470.
No bands.	No bands.	2 bands.
464 mm.	**614 mm.**	**744 mm.**
λ.	λ.	λ.
2590 v.w. 2530 ,,	2590 w. 2530 w.	2590 w. 2530 w.
General absorption at λ 2470.	Both bands stronger than at 464 mm. General absorption at λ 2490.	Both bands stronger than at 614 mm. General absorption at λ 2500.
2 bands.	2 bands.	2 bands.

The vapour of thiophen was also examined in a column 100 mm. long at a constant temperature of 14° and under varying pressures. The three weak bands described in table V were not seen; but three wide bands were observed in the more refrangible regions which are hidden by the general absorption in the 200 mm. tube.

TABLE VII.

The absorption bands of thiophen vapour in a column 100 mm. long at a constant temperature of 14° and under varying pressures.

14 mm.	164 mm.	460 mm.	744 mm.
λ.	λ.	λ.	λ.
2416 wide band, about 0·5 A.U. wide 2406 wide band, about 0·7 A.U. wide 2395 wide, w.	2416 wide 2406 ,, 2395 ,, , stronger than at 14 mm.	2415 wide 2406 ,, 2395 ,,	2415 wide 2406 ,, 2395 ,,
Absorption of rays from λ 2390 to Cd 2329, Cd lines 2321 to 2265 well marked.	Absorption of rays from λ 2375 to Cd 2329; the Cd lines from 2329 to 2239 were visible.	Absorption of rays from λ 2375 to Cd 2329.	General absorption began at λ 2390, the Cd lines 2329 to 2265 being visible.
3 bands.	3 bands.	3 bands.	3 bands.

From the above tables relating to thiophen vapour, it will be noticed that in the 200 mm. tube at the higher temperatures and pressures two weak and rather narrow bands were observed at 2590 and 2530, and that in the 100 mm. tube these bands were too weak to be seen, but three wide weak bands were visible, which were covered by the general absorption of the greater mass of vapour in the 200 mm. tube.

TABLE VIII.

Pyrrole.—The absorption bands of pyrrole in a column 200 mm. long at a constant temperature of 17·5° and under varying pressures. Abbreviations as before.

746 mm.	466 mm.	166 mm.	16 mm.
λ.	λ.	λ.	λ.
2590 w.	2590 w.	2590 v.w.	All the rays were transmitted to λ2265; the Cd lines 2194 and 2144 visible.
2530 w.	2530 w.	2530 ,,	
2495 w., wide	2595 w., wide	2495 ,,	
2481 ,,	2481 ,,	2481 ,,	
		2470 ,,	
General absorption from λ 2475.	General absorption from λ 2460.	General absorption from λ 2440.	
4 bands.	4 bands.	4 bands.	No bands.

The vapour was also examined in a column 200 long at a constant temperature of 100° and under pressures varying from 16 mm. to 746 mm., but no bands were observed.

The above table shows the presence of two narrow weak bands at 2590 and 2530, and three weak wide bands at 2495, 2481, 2470, in the vapour of pyrrole.

Solutions.

Furan.—Hartley and Dobbie (Trans., 1898, **73**, 598) examined alcoholic solutions of varying strengths, but they found no absorption bands. The author has examined alcoholic solutions of different strengths, and through varying thicknesses, but no bands were observed. The following numbers represent the positions where general absorption began through various thicknesses of the solutions.

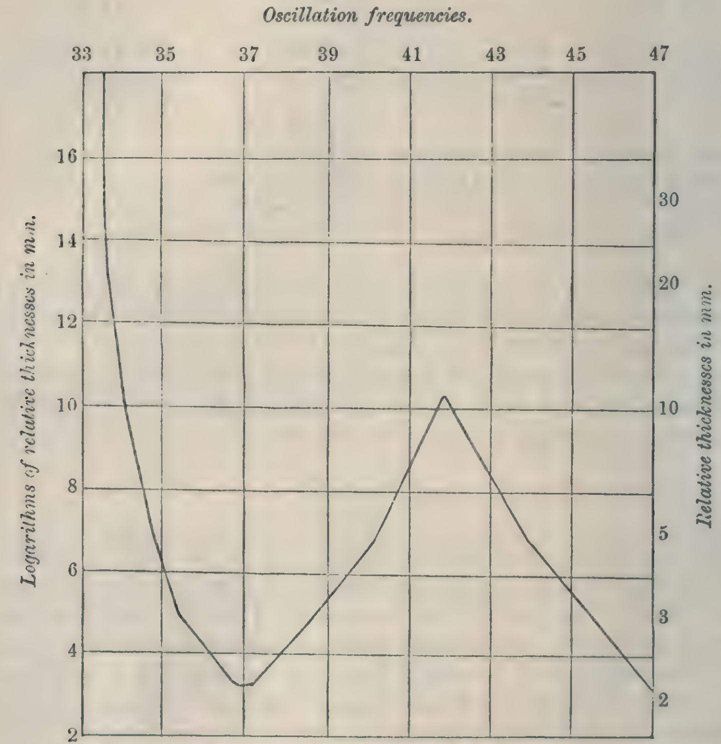
N/10-solution : 2 mm. thick : general absorption began at λ 2300.
30 ,, ,, ,, ,, ,, λ 2780.
N/100-solution : 2 ,, ,, ,, ,, ,, λ 2260.
30 ,, ,, ,, ,, ,, λ 2380.
N/1000-solution : 2 ,, ,, ,, ,, ,, λ 2180.
30 ,, ,, ,, ,, ,, λ 2280.

Furfuraldehyde.—Hartley and Dobbie (*loc. cit.*) stated that alcoholic solutions did not exhibit any absorption bands. When 0·096 gram was dissolved in alcohol, general absorption began at λ 3087 through 1 mm. thick, and at λ 3723 through 25 mm. thick.

The author examined *N*/10- and *N*/100-solutions, but no bands were observed, and the following numbers represent the positions where general absorption began:

N/10-solution : 2 mm. thick : general absorption began at λ 3120.
30 ,, ,, ,, ,, ,, λ 3590.
N/100 solution : 2 ,, ,, ,, ,, ,, λ 2970.
30 ,, ,, ,, ,, ,, λ 3160.

In examining a *N*/1000-solution, however, a large band was discovered, the absorption curve of which has been drawn (Fig.).



N/1000-*solution of furfuraldehyde in alcohol.*

Thiophen.—Hartley and Dobbie (*loc. cit.*) found that there were no bands in any of the alcoholic solutions they used, but that the latter were very transparent. The author has examined the following solutions, but no bands were observed:

N/10-solution : 2 mm. thick : general absorption began at λ 2500.
30 ,, ,, ,, ,, ,, λ 2560.
N/100-solution : 2 ,, ,, ,, ,, ,, λ 2460.
30 ,, ,, ,, ,, ,, λ 2510.
N/1000-solution : 2 ,, ,, ,, ,, ,, λ 2195.
30 ,, ,, ,, ,, ,, λ 2470.

Pyrrole.—Hartley and Dobbie (*loc. cit.*) found no bands in any of the alcoholic solutions of varying strengths and thicknesses that they employed. Coblentz (*Astrophys. J.*, 1904, **20**, 207) found a band in the ultra-red regions of the spectrum at 2·94μ. The author has examined alcoholic solutions of various strengths, but no bands were observed in the ultra-violet.

N/10-solution :	2 mm.	thick :	general	absorption	began at	λ 2380.
	30 ,,	,,	,,	,,	,,	λ 2645.
N/100-solution :	2 ,,	,,	,,	,,	,,	λ 2295.
	30 ,,	,,	,,	,,	,,	λ 2425.
N/1000-solution :	2 ,,	,,	,,	,,	,,	λ 2195.
	30 ,,	,,	,,	,,	,,	λ 2325.

Liquids.—The liquids furfuraldehyde and pyrrole were also examined. For this purpose, a drop of the liquid was pressed between two thin quartz plates, and held in front of the slit of the spectroscope, whilst the light of the Cd spark was passed through for five minutes. No bands were observed, and the regions where general absorption began were:

	λ.
Furfuraldehyde	3130
Pyrrole	2320
Thiophen (Pauer)	2540

General Results and Discussion.

The more important results of the preceding investigations are that:

(1) The vapour of furan exhibits absorption bands, some of which are very similar in appearance and have similar differences in wave-lengths. The vapour of furfuraldehyde exhibits bands, most of which can be grouped together in having similar differences both in appearance and in wave-lengths, but which are different from those of furan. The vapours of thiophen and pyrrole show a few bands, two of which are comparable with two in the vapours of furan and furfuraldehyde.

(2) Alcoholic solutions of various strengths of furan, thiophen, and pyrrole show no absorption bands, whilst *N*/1000-solution of furfuraldehyde exhibits a strong band in the ultra-violet. The liquids, furfuraldehyde, thiophen, and pyrrole, have no absorption bands.

The author has already compared and discussed the results of a comparative study of the vapours, liquids, and solutions of various substances (*loc. cit.*). The present investigation confirms generally the conclusions that the selective absorption by the molecules of any substance is conditioned not only by the type and orientation of the atoms, but also by the physical conditions, as vapours, liquids, or in solution.

With regard to the solutions, it is remarkable that furan, pyrrole, and thiophen are so transparent, and that furfuraldehyde exhibits so large a band. The many bands found in the vapour of the latter substance disappear, and their place is taken by one large band. The comparative transparency of the vapours of pyrrole and thiophen, on the other hand, is comparable with that of the solutions. The possible influence of the solvent on the vibrations of dissolved molecules, as well as the absence of bands in liquids, has been discussed in the previous papers (*loc. cit.*).

Considering the vapours, it is clear that the vibrations of the atoms of the furan molecule are wholly different from those of the thiophen and pyrrole molecules. The substitution of oxygen by sulphur or the NH-group has completely altered the oscillations or vibrations which produce selective absorption. The thiophen and pyrrole vapours are transparent as compared with furan and furfuraldehyde, and there are only two bands common to them all. The series of phenomena may be compared by considering the influence of the oxygen atom on the vibrations of the other atoms of the ring. The oxygen atom appears to be the controlling influence, for the vapours of furan and furfuraldehyde have a considerable number of bands; and these bands are absent, with two exceptions, from the vapours of thiophen and pyrrole, in which the oxygen atom is replaced by sulphur and the NH-group respectively. In this direction the results may be discussed from the point of view of valency, and how far the changing valencies of sulphur and nitrogen are responsible for the remarkable absence of bands in the vapours of thiophen and pyrrole, as compared with furan and its aldehydic derivative. In the case of furan and its derivative the normal valency of oxygen is saturated, and the vapours exhibit a considerable number of bands, whereas in thiophen and pyrrole the valencies of the sulphur and nitrogen atoms are not saturated, and there are only a few bands in the vapours of these substances. Considering a single molecule of furan, and assuming the saturation of the valency of the oxygen atom to be normal and complete, the molecule would be more stable, more elastic, and more frequently periodic in its vibrations, because its energy may be considered to be wholly contained within the single system. On the other hand, in pyrrole or thiophen, the energy would not be wholly contained within the molecule, because the valency of the sulphur or the nitrogen atom is not at its maximum saturation. Part of the energy is employed externally to the single molecular system, and, as a result, the molecule does not possess the stability or the elasticity of the furan molecule; the regular periodicity of its vibrations is small in comparison, and the bands are fewer in number and generally different in position.

Nevertheless, it is not sufficient to explain satisfactorily the differences in the absorption bands from valency considerations alone. For example, Baker and Baly (Trans., 1907, **91**, 1122) explained the absence of bands in the ultra-violet regions of solutions of piperidine by considering the saturation of the various atoms; but, as the author has pointed out (this vol., p. 692), the presence of the many bands in the vapour of piperidine is opposed to such an explanation. Nor is it sufficient to isolate any particular atom, or group of atoms, in a molecule, and consider these alone as the primary agents in any vibrations producing selective absorption. The introduction of a single atom in a molecule must affect the movements of all the atoms; and the vibrations of all the atoms are concerned in the final result. The forces which influence these lie both inside and outside the molecule. They include such factors as valency, mass, the nature of the ring system and its side-chains, and the physical conditions as vapours or in solutions; and, in view of the corpuscular theory of the atom, a complete explanation of the origin of selective absorption implies a consideration of many and deep-seated factors.

I have again to thank the Government Grant Committee of the Royal Society, by whose assistance the greater part of the cost of the apparatus employed in this investigation was defrayed.

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CLV.—*The Oxidation of Monohydric Phenols with Hydrogen Peroxide.*

By GEORGE GERALD HENDERSON and ROBERT BOYD, B.Sc. (Carnegie Research Scholar).

HAVING occasion to prepare some dihydric phenols of the formula $C_{10}H_{12}(OH)_2$, we endeavoured to find a simpler and more direct method of obtaining these compounds from monohydric phenols than those which are usually employed. To begin with, we applied to thymol the process of oxidising monohydric phenols in alkaline solution with potassium persulphate, which is stated to work well with the lower members of the series, but the results were not satisfactory. Equally disappointing results attended our trials of the method of oxidation with dilute solutions of hydrogen peroxide, but the use of Merck's "perhydrol," a 30 per cent. aqueous solution of hydrogen peroxide, led to the attainment of the desired end. A number of monohydric phenols of the benzene series were treated with this reagent, glacial acetic acid being used as a solvent for the phenol, and all were found to undergo oxidation more or less easily, either in the cold or when moderately heated. The product was either a quinone, from which, of course, the corresponding dihydric phenol could be obtained by reduction, or a dihydric phenol, or, in one or two cases, a tetrahydric phenol. The following is a statement of the phenols examined and of the products obtained from them under the conditions described below.

Thymol gave a very good yield of thymoquinone, along with a small quantity of a new tetrahydric phenol, *tetrahydroxycymene*, $C_6MePr^{\beta}(OH)_4$, a colourless, crystalline solid, melting at 168°.

Carvacrol gave the same products as thymol, in approximately the same relative proportions.

3 : 5-Diethylphenol, $C_6H_3Et_2\cdot OH$, gave, apparently as sole product, the corresponding 3 : 5-*diethyl*-p-*benzoquinone*, $C_6H_2Et_2O_2$, golden-yellow needles, melting at 36°, from which, by reduction with sulphurous acid, the dihydric phenol, 3 : 5-*diethylquinol*, $C_6H_2Et_2(OH)_2$, was obtained in colourless crystals, melting at 114°. p-*Nitroso*-3 : 5-*diethylphenol* was also prepared. It forms pale yellow crystals, melting at 136°, and on reduction and subsequent oxidation yields diethyl-*p*-benzoquinone.

p-tert.-Butylphenol, $C_6H_4(CMe_3)\cdot OH$, gave a new tetrahydric phenol, *tetrahydroxy*-tert.-*butylbenzene*, $C_6H(CMe_3)(OH)_4$, which crystallises in slender, colourless needles, melting at 138°.

Phenol gave quinol, a little *p*-benzoquinone, and a little catechol; no resorcinol was found.

o-Cresol gave toluquinol (2 : 5-dihydroxytoluene) and some toluquinone; *m*-cresol gave toluquinol, some toluquinone, and a little orcinol; and *p*-cresol gave homocatechol (3 : 4-dihydroxytoluene); no other product was found.

The character of the oxidation products obtained depended, in the first place, on the constitution of the phenol oxidised, and, in the second place, on the conditions of the experiment, namely, the proportion of perhydrol used, the concentration of the acetic acid solution, the temperature, and the time. As regards the first point, it was found that monohydric phenols, in which the *p*-position relative to the hydroxyl radicle is unoccupied by a radicle other than hydrogen, are more or less easily attacked by hydrogen peroxide even at the ordinary temperature, and that the product of oxidation is mainly a quinone, or a *p*-dihydric phenol, or a mixture of both, according to the conditions under which the reaction is carried out. On the other hand, those monohydric phenols in which the *p*-position relative to the hydroxyl group is occupied are oxidised with greater difficulty, and a higher temperature is necessary; in such cases the product is usually a dihydric phenol containing the hydroxyl groups in the *o*-position with respect to each other. The lower members of the series tend to give tarry products more easily than the higher members, and it is best to use a larger proportion of the solvent (acetic acid) when the former are being oxidised.

We have also examined the action of perhydrol on some cyclic hydrocarbons. In each case the hydrocarbon was mixed with perhydrol, sufficient acetic acid to form a clear solution was added, and the liquid was left for some time at the ordinary temperature or gently heated. The members of the benzene series which were used, namely, benzene, toluene, 1 : 3-diethylbenzene, and cymene, did not appear to react at all easily with the oxidising agent, but naphthalene, anthracene, and phenanthrene were readily oxidised, yielding phthalic acid, anthraquinone, and phenanthraquinone respectively.

The course of the preparative work involved in this investigation led us to attempt to prepare higher dihydric phenols directly by condensing quinol and resorcinol with diethyl ether in presence of anhydrous aluminium chloride. These experiments were unsuccessful, but we found that phenol could be condensed with methyl propyl ether, yielding a substance which appears to be a *methylpropylphenol*, $C_6H_3MePr\cdot OH$.

We intend to continue to study the behaviour of hydrocarbons towards perhydrol, and also to extend our experiments to derivatives of phenols and to phenols other than those of the benzene series.

EXPERIMENTAL.

According to a patented process (D.R.-P. 81068 and 81298), dihydric phenols of the benzene series can be obtained on the manufacturing scale from monohydric phenols by means of potassium persulphate. The persulphate is added in small portions to a dilute alkaline solution of the phenol, and the liquid is kept for one or two days at the ordinary temperature, or at 40°. When the reaction is finished, the solution is saturated with carbon dioxide, any unchanged phenol is distilled off in a current of steam, the residual liquid is acidified with dilute acid and then boiled, and finally the dihydric phenol which has been formed is extracted with ether. If the *p*-position relative to the hydroxyl group in the monohydric phenol is free, a *p*-dihydroxy-compound is obtained, but if the *p*-position is occupied, the product contains two hydroxyl groups in the *o*-position with respect to each other. Thus, phenol yields quinol, whilst *p*-cresol yields homocatechol.

As the process appeared to be a practicable one, we applied it in the prescribed manner to the oxidation of thymol, but found that with that compound the reaction does not proceed smoothly, as in the case of lower phenols. Much of the thymol remained unattacked, whilst the rest was mainly converted into a tarry substance, from which it was scarcely possible to separate any definite oxidation product. Various modifications of the process were tried—such as keeping the mixture cool with ice; adding the persulphate to a solution of thymol in the least possible quantity of alkali, and maintaining the mixture slightly alkaline by addition of sodium carbonate from time to time; agitating a mixture of thymol with aqueous potassium persulphate for several days, both at the ordinary temperature and at 60°—but with no improvement in the results.

A dilute solution of hydrogen peroxide, either with or without the addition of a small quantity of an iron salt, has frequently been used as an oxidising agent, and, according to Martinon (*Bull. Soc. chim.*, 1885, [ii], **43**, 155), when dilute aqueous hydrogen peroxide is gradually added to pure phenol in the cold, and the liquid is subsequently heated to 90°, oxidation of the phenol takes place, and a mixture of quinol, *p*-benzoquinone, and catechol is obtained. With thymol, however, we found this process also to be unsatisfactory; using ordinary "ten volume" hydrogen peroxide, according to Martinon's method, very little of the thymol was attacked, even when the mixture was heated. It then occurred to us to try a stronger solution of hydrogen peroxide, and this led to success. It was found that thymol and other monohydric phenols, when dissolved in glacial acetic acid, are more or less readily oxidised by perhydrol, with the results described in the following pages.

Oxidation of Thymol with Perhydrol.—Seventy-five grams of thymol (1 mol.) were mixed with 190 c.c. of perhydrol (about 2 mols.), sufficient acetic acid was added to hold the thymol in solution, and the mixture was kept at the ordinary temperature. After a week or two, a small quantity of a colourless, crystalline solid had separated from the solution. The solid was collected, and water was gradually added to the filtrate until no further precipitation took place. The yellow, crystalline precipitate was agitated with dilute sodium hydroxide, when only a small part passed into solution, and the undissolved portion was collected, washed with water, and dried. The golden-yellow crystals obtained in this way melted at 45·5°, and were identified as thymoquinone.

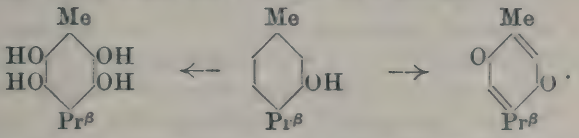
A small additional quantity of thymoquinone was obtained from the mother liquor by steam distillation. Only a little of the thymol remained unoxidised.

The alkaline solution with which the thymoquinone had been washed gave, on acidification, a precipitate of a crystalline compound, which proved to be identical with the substance which had crystallised from the original acetic acid solution. After purification by recrystallisation from dilute alcohol, it was dried and analysed:

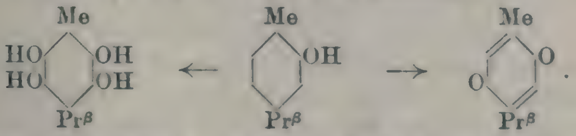
0·1562 gave 0·3460 CO_2 and 0·0947 H_2O. $C=60·4$; $H=6·7$.
0·1544 ,, 0·3399 CO_2 ,, 0·0992 H_2O. $C=60·1$; $H=7·1$.
$C_{10}H_{14}O_4$ requires $C=60·6$; $H=7·1$ per cent.

Tetrahydroxycymene, $C_6MePr^{\beta}(OH)_4$, so obtained, forms small, colourless crystals, which melt at 168°. If exposed to the air in a moist state, it begins to turn yellow. It is rather sparingly soluble in cold water, readily so in alcohol, ether, chloroform, or glacial acetic acid. It dissolves with ease in solutions of alkali hydroxides, and the colourless liquid quickly begins to acquire a brown coloration in contact with air. In an aqueous solution, ferric chloride produces a bulky, red precipitate.

The chief product of the oxidation of thymol by perhydrol is thymoquinone, whilst tetrahydroxycymene is only formed in small proportion. Very little tarry matter is produced.

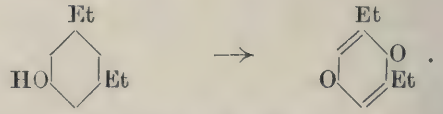


Oxidation of Carvacrol with Perhydrol.—The oxidation was carried out in the same way as in the case of thymol, and, as was to be expected, the result was precisely similar. The chief product was thymoquinone, and, in addition, a small quantity of tetrahydroxycymene was formed. Only a little tarry matter was produced, and almost all the carvacrol was oxidised.



Oxidation of 3:5-*Diethylphenol with Perhydrol*.—The diethylphenol required for this experiment was prepared by Jannasch and Rathjen's method (*Ber.*, 1899, **32**, 2392), which gave a satisfactory yield.

The diethylphenol was oxidised with perhydrol in the same way as thymol. When the reaction appeared to be completed, the solution was diluted with water, and the yellow crystals, which separated after some time, were collected and purified by crystallisation from dilute alcohol. Examination of the properties of the compound showed it to be 3:5-*diethyl*-p-*benzoquinone*, $C_6H_2Et_2O_2$, which, for purposes of comparison, we had already prepared by another method described below. The filtrate was neutralised with sodium carbonate and agitated with ether, the ethereal solution was washed and dried, and after removal of the ether by distillation a dark red, oily residue was obtained. The oily substance was shaken up with water, and after a short time the greater part solidified. The crystals were collected and drained on a porous plate, and, after recrystallisation, proved to be a further quantity of diethyl-*p*-benzoquinone. The small quantity of oily matter which was produced along with the quinone was not further examined.



Diethyl-*p*-benzoquinone was also prepared from diethylphenol by a less direct method.

p-*Nitroso*-3:5-*diethylphenol*, O:$C_6H_2Et_2$:NOH (*diethyl*-p-*benzoquinoneoxime*), was first obtained as follows. Diethylphenol was dissolved in alcohol previously saturated with hydrogen chloride, the solution was cooled with ice, and a cooled concentrated aqueous solution of the calculated quantity of sodium nitrite was slowly added. The dark green liquid obtained in this way was poured into water, when a yellowish-brown solid was precipitated. The precipitate was collected, washed with water, dried, washed with a little chloroform, and recrystallised from dilute alcohol. It forms small prisms of a pale yellow colour, which melt and decompose at 136°. It is readiy soluble in alcohol, and almost insoluble in water:

0·1940 gave 13 c.c. N_2 at 15° and 760 mm. N = 7·84.
0·3920 ,, 26·4 c.c. N_2 at 20° and 760 mm. N = 7·7.
$C_{10}H_{13}O_2N$ requires N = 7·8 per cent.

3:5-*Diethyl*-p-*benzoquinone*, O:$C_6H_2Et_2$:O, was prepared from nitrosodiethylphenol in the following manner. Five grams of the nitroso-compound were dissolved in 50 grams of 10 per cent. ammonia, and the solution was saturated with hydrogen sulphide. The reduction product, *p*-aminodiethylphenol, was precipitated as a white solid, which was collected and washed with water. The precipitate was dissolved in 90 c.c. of 3 per cent. sulphuric acid, and 100 c.c. of water and 50 c.c. of a 10 per cent. solution of potassium dichromate were added. After about half an hour, the precipitate which had formed was collected and dissolved in glacial acetic acid, and small quantities of chromic anhydride were added to the solution from time to time until the oxidation was completed. The quinone was then precipitated with water, collected, washed with water, and purified by crystallisation from dilute alcohol. It forms slender needles of a golden-yellow colour, which melt at 36°. If it is allowed to separate slowly from solution, crystals several centimetres in length may be obtained. It is only slightly soluble in water, but easily so in alcohol or ether, and it volatilises readily in a current of steam:

0·1967 gave 0·5294 CO_2 and 0·1240 H_2O. $C=73·4$; $H=7·0$.
$C_{10}H_{12}O_2$ requires $C=73·2$; $H=7·3$ per cent.

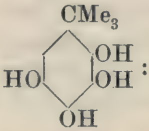
The corresponding dihydric phenol, 3:5-*diethylquinol*, $C_6H_2Et_2(OH)_2$, was prepared by reduction of the quinone with sulphurous acid. The quinone was gently warmed with aqueous sulphurous acid until all the solid had passed into solution, and the reduction appeared to be completed. The phenol was then extracted with ether, and the ethereal solution was washed with water, dried, and concentrated to small bulk. On cooling, the phenol separated in small, colourless crystals. It melts at 114°, and is fairly easily soluble in water, and readily so in alcohol or ether. A solution in alkali hydroxides is at first colourless, but quickly turns brown on exposure to air. In aqueous solution the phenol is readily oxidised by ferric chloride, yielding the quinone:

0·2707 gave 0·7145 CO_2 and 0·2073 H_2O. $C=72·0$; $H=8·6$.
$C_{10}H_{14}O_2$ requires $C=72·3$; $H=8·4$ per cent.

Oxidation of p-tert.-*Butylphenol*, $C_6H_4(CMe_3)·OH$, *with Perhydrol*.—The phenol required for this experiment was prepared from *tert*.-butylbenzene. Nitration of the hydrocarbon yielded a mixture of the solid *p*- with some of the liquid *o*-nitro-derivative. The *p*-nitro-compound was separated and reduced by means of tin and hydrochloric acid. The oily *p*-amino-compound was diazotised, and on distilling the solution with steam, a satisfactory yield of the phenol was obtained in lustrous needles, which melted at 98° (compare Studer, *Ber*., 1881, **14**, 1472).

Five grams of the phenol were mixed with 10 grams of perhydrol and the quantity of acetic acid required to form a clear solution. In this case the reaction appeared to proceed very slowly at the ordinary temperature, hence the solution was heated at about 60° for several days, and then neutralised with sodium carbonate and agitated with ether. The ethereal solution was washed with water, dried, and after removal of the ether by distillation, a white, solid residue was left, which was recrystallised from dilute alcohol. The substance thus obtained was found on analysis to be *tetrahydroxy-*

tert.-*butylbenzene*, $C_6H(CMe_3)(OH)_4$. It crystallises in slender, colourless needles, which melt at 138°. It dissolves rather sparingly in water, but freely in alcohol or ether and in solutions of alkalis. Ferric chloride does not produce a coloration in an aqueous solution. The probable constitution of the compound is shown by the formula

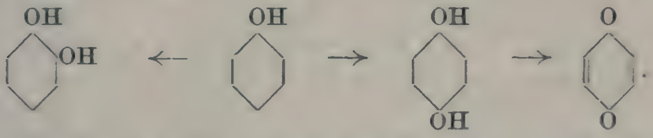


0·1179 gave 0·2602 CO_2 and 0·0764 H_2O. $C=60·2$; $H=7·2$.
$C_{10}H_{14}O_4$ requires $C=60·6$; $H=7·1$ per cent.

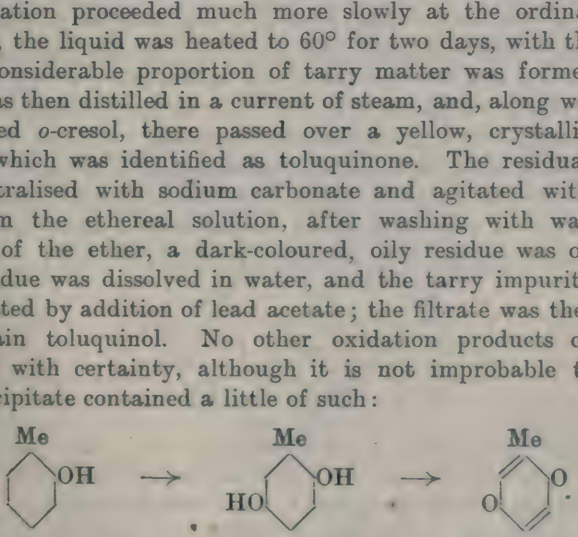
From the mother liquor from which the tetrahydric phenol had crystallised, a small quantity of another colourless, crystalline *compound* was isolated. This substance melts at 58°, and is sparingly soluble in water, but readily so in solutions of alkalis. There was, however, too little in our hands for identification. Not much tarry matter was formed, and practically all the butylphenol was oxidised. We expected to get a dihydric phenol (3:4-dihydroxybutylbenzene) as the chief product, but probably the fact that the mixture was heated for some time accounts for the formation of the more highly oxidised compound. A repetition of the experiment at a lower temperature may yield the dihydric phenol.

Having obtained these results with phenols of the formula $C_{10}H_{13}\cdot OH$, it appeared of interest to investigate the behaviour towards perhydrol of some of the lower members of the series, and we selected as examples phenol and *o*-, *m*-, and *p*-cresols. Preliminary experiments showed that these compounds are more susceptible to the action of the oxidising agent than thymol and the other higher phenols examined, and that in order to prevent the formation of considerable quantities of tarry matters it was necessary to avoid using excess of perhydrol, to dilute the mixture with a larger proportion of acetic acid, and usually to carry out the oxidation at the ordinary temperature.

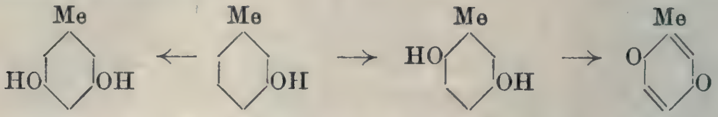
Oxidation of Phenol with Perhydrol.—The phenol was mixed with perhydrol in such quantity that about 1 mol. of hydrogen peroxide was present for each mol. of phenol, and about twice the quantity of acetic acid necessary to keep the phenol in solution was added. After keeping for several days at the ordinary temperature, a crop of crystals had separated from the solution. The solid was collected, purified, and proved to consist of quinol, by determination of its melting point, 169°, and by its easy conversion into *p*-benzoquinone by oxidation with ferric chloride in aqueous solution. The liquid from which the crystals of quinol had been removed was distilled with steam, when a little *p*-benzoquinone passed over and was collected. The residual liquid gave a precipitate when mixed with lead acetate. The first portion of the precipitate, which was very impure, was rejected; the rest was collected and decomposed with dilute sulphuric acid. The filtrate from the lead sulphate was agitated with ether, and from the ethereal solution a solid which gave all the reactions of catechol was obtained. A further quantity of quinol was obtained from the liquid from which the lead salt of catechol had been separated, but no resorcinol could be detected. Thus, with the strong solution of hydrogen peroxide, the oxidation products from phenol were the same as those obtained by Martinon (*loc. cit.*) by the use of a dilute solution:



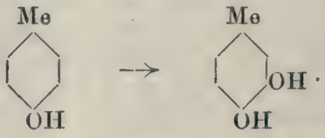
Oxidation of o-*Cresol with Perhydrol.*—The conditions of the experiment were the same as in the case of phenol, except that as the oxidation proceeded much more slowly at the ordinary temperature, the liquid was heated to 60° for two days, with the result that a considerable proportion of tarry matter was formed. The liquid was then distilled in a current of steam, and, along with some unchanged *o*-cresol, there passed over a yellow, crystalline compound, which was identified as toluquinone. The residual liquid was neutralised with sodium carbonate and agitated with ether, and from the ethereal solution, after washing with water and removal of the ether, a dark-coloured, oily residue was obtained. This residue was dissolved in water, and the tarry impurities were precipitated by addition of lead acetate; the filtrate was then found to contain toluquinol. No other oxidation products could be detected with certainty, although it is not improbable that the lead precipitate contained a little of such:



Oxidation of m-*Cresol with Perhydrol.*—The oxidation was carried out precisely as in the case of phenol. After being kept for a sufficient time, the liquid was distilled in a current of steam, and the distillate was found to contain toluquinone, together with some unchanged *m*-cresol. The residual liquid was filtered in order to remove some tarry matter which was present, lead acetate was added to the filtrate, and the lead salt, which was precipitated, was collected. The filtrate was agitated with ether, and toluquinol was obtained on concentration of the ethereal extract. The lead salt was decomposed with dilute sulphuric acid, and the filtrate from the lead sulphate yielded to ether a substance with the reactions of orcinol:



Oxidation of p-*Cresol with Perhydrol.*—Preliminary experiments showed that *p*-cresol was not oxidised by perhydrol nearly so easily as *o*- or *m*-cresol, and consequently the mixture of *p*-cresol, perhydrol, and acetic acid was heated at about 60° for three days. The greater part of the acetic acid was then neutralised with sodium carbonate, and the oily liquid which was thrown out of solution was separated. The aqueous liquid gave no precipitate with lead acetate, which indicated the absence of *iso*orcinol. It was agitated with ether, and after the ethereal solution had been washed, the ether was removed by distillation, and an oily residue was left. This was mixed with the oily substance which had already been obtained, and the mixture was distilled. A large portion of the distillate proved to be unchanged *p*-cresol, but the fraction, which boiled at 240—255°, yielded on redistillation a syrupy liquid, which gave the characteristic reactions of homocatechol (3: 4-dihydroxytoluene)—reduction of Fehling's solution and of ammoniacal silver nitrate in the cold, and with ferric chloride a green coloration which turned brown after some time. Homocatechol was the only oxidation product detected:



Attempted Condensation of Resorcinol and of Quinol with Diethyl Ether.—In view of the fact that diethylphenol was readily obtained by condensing phenol with ether with the aid of anhydrous aluminium chloride, we thought it desirable to attempt to prepare corresponding dihydric phenols by a similar direct method. Accordingly, a mixture of resorcinol with ether was treated with aluminium chloride in the manner described by Jannasch and Rathjen (*loc. cit.*). Only a slight reaction appeared to take place even when the mixture was heated, and when the product was treated with water and worked up in the usual way, practically nothing but unchanged resorcinol was obtained. An attempt to condense quinol with ether was equally unsuccessful, and it is evident that these dihydric phenols do not undergo condensation with ether under the same conditions as lead to the formation of diethylphenol.

Condensation of Phenol with Methyl Propyl Ether.—In order to ascertain whether the reaction between phenol and diethyl ether could be extended to other ethers, we prepared some methyl propyl ether, and condensed it with phenol in the following manner. Thirty grams of phenol were dissolved in an equal weight of pure ether, the solution was cooled, and 120 grams of anhydrous aluminium chloride were slowly added in small portions. The mixture was then heated at 140° until no more hydrogen chloride was evolved, and, after cooling, the mass was decomposed with water and the oily product extracted with ether. The ethereal solution was washed and dried, the ether removed, and the residue distilled. A little unchanged phenol passed over first, but the bulk of the product distilled at 130—140°. On redistillation of this fraction, an oily liquid, boiling at about 135°, was obtained. It is sparingly soluble in water, but easily so in alcohol or ether and in solutions of alkali hydroxides, and in aqueous solution it gives a dark green coloration with ferric chloride. Probably this compound is a *methylpropylphenol*, $C_6H_3MePr\cdot OH$. We propose to study the condensation of monohydric phenols with ethers more fully.

We take this opportunity of expressing our thanks to the Research Fund Committee of the Carnegie Trust for a grant which defrayed the expenses of this investigation.

Chemistry Department,
The Glasgow and West of Scotland Technical College.

CLVI.—*The Relation between Solubility and the Physical State of the Solvent in the Case of the Absorption of Carbon Dioxide in* p-*Azoxyphenetole.*

By Ida Frances Homfray, D.Sc.

There appears to be, at the present time, a considerable amount of evidence to show that solution is, in general, a property of the amorphous, as distinguished from the crystalline, form of matter. As, however, this evidence is somewhat scattered, it is perhaps not undesirable to collate some of the more salient points.

A solution, in its widest sense, may be taken to mean a homogeneous phase of two or more components in variable proportions; it may be present in the gaseous, liquid, or solid state.

Solutions in the normal liquid phase can exist in equilibrium with almost all solids, liquids, and gases, and the same may be said of the gaseous phase, for the vapours of liquids and solids are all completely miscible.

When, however, we consider mixtures in the solid phase, we find that a definite distinction must be drawn between the amorphous and the crystalline forms.

The presence of directive forces and the formation of crystal faces appear almost entirely to prevent molecular interpenetration, mixtures of variable proportions being practically confined to isomorphous substances.

Thus, a finely divided crystalline precipitate is generally pure and easily freed from solution and moisture, whereas an amorphous precipitate always carries down with it both liquid and solid impurities in a state of intimate mixture indistinguishable from true solution, and, after drying, reabsorbs moisture from the air.

As has been pointed out by Roozeboom and others, no logical distinction can be drawn between the liquid and solid states, unless the latter term is restricted to the crystalline condition. Glass, a typically amorphous substance, can pass by gradual transition from the mobile liquid form, through all stages of viscosity, to a condition of mechanical rigidity, no triple point occurring in the system, which consists throughout of two phases only: vapour (negligible in this case) and congealing fluid. In this condition it must therefore be considered as a highly supercooled fluid. Like other fluids, it is capable of dissolving foreign substances, notably the metallic oxides used as colouring matter.

If, however, crystallisation sets in, it proceeds continuously without external agency to completeness, the supercooled state being a metastable one, and at the same time dissolved matter is separated from the crystals. The results are seen in some ancient stained glass windows, where devitrification is slowly, but irremediably, proceeding.

The same distinction is very well exemplified by many of the igneous rocks, crystals of pure minerals being surrounded by an isotropic glassy matrix of homogeneous structure, but consisting of a solution of indefinite composition in the supercooled fluid state.

The gradual penetration of crystalline metals by gold appears at first sight to indicate solution in the crystalline state. The experiments have, however, been conducted under very high pressure, and both Ewing and Spring have shown that something approaching liquefaction occurs on the surface of metals exposed to frictional pressure; the same probably takes place throughout the metal when under great stress, progressive solution of other metals accompanying it and producing uniform distribution.

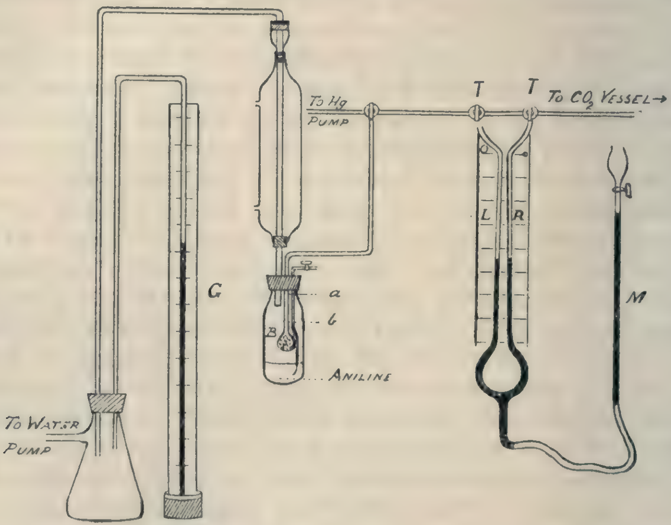
The equilibria between gases and solids present many interesting points, but have not received much attention, except in the case of the absorption of hydrogen by palladium and platinum. It appears still uncertain whether this is a case of true solution or of an unstable chemical compound, the absorption being entirely selective, and taking place only at high temperatures.

It has long been known that fused silver dissolves considerable quantities of oxygen, retaining it while in the supercooled state. On crystallising, the gas is evolved with considerable violence. Quite recently this phenomenon has been qualitatively investigated, together with the explosive crystallisation of antimony, due to the same cause (Sieverts, *Zeit. physikal. Chem.*, 1909, **68**, 115). A curious case of the formation of air bubbles expelled from solution on the devitrification of glass slag has, I believe, been brought to the notice of geologists on the north-west coast of England, where the floating glass was washed up and at first mistaken for the product of submarine volcanic action. At low temperatures, amorphous nickel oxide can dissolve considerable quantities of gas, and the quantitative study of the laws governing the equilibria between charcoal and various gases has led the author (*Proc. Roy. Soc.*, 1910, *A*, **84**, 99) to the conclusion that the absorption is to be attributed rather to solution in the highly supercooled fluid than to surface condensation. Also, on heating the charcoal to a high temperature, its absorptive power is permanently much reduced, probably owing to partial crystallisation, for, on converting it completely into graphite, the property is entirely lost.

In view of the foregoing considerations, it is obviously of considerable interest to investigate the solubility of gases in substances which can exist, between definite temperature limits, in the rigid crystalline, liquid crystalline, and isotropic liquid forms. For, according to this view, the two first phases must both be classed as solids, and may be expected to have considerably smaller solvent power than the isotropic liquid. It has been shown by Schenck (*Zeit. physikal. Chem.*, 1898, **25**, 337) that isotropic liquids are not miscible with the crystalline liquid phase; the present investigation is therefore confined to the question of the solubility of gases, carbon dioxide being the most suitable.

These phases are produced at successively higher temperatures, and if, therefore, either or both changes of phase is accompanied by a considerable increase of gas absorption, the temperature-pressure diagram should show definite maxima and minima. It appears from the researches of Lehmann, and more recently of Vorländer, Hulett, Schenck, and others, that there is little reason to doubt the truly crystalline structure of the anisotropic liquid.

The first experiments to be described were carried out with *p*-azoxyphenetole (obtained direct from Kahlbaum and recrystallised), and, in spite of the comparatively high melting and clearing points (156·5° and 161·7°), and consequent very small actual volume of gas dissolved, well marked maxima and minima were consistently recorded in the numerous series of measurements under slightly modified conditions which were required before quantitative results were obtained. It was, of course, also necessary to prove conclusively that no chemical action takes place, even at the highest temperatures required.



The apparatus used is shown in the accompanying diagram.

The differential manometer *L*,*R*, as well as the connecting tubes to the experimental bulb *B* and the gas-holder, were of thick-walled glass tubing of 2 mm. bore. The two manometer taps *T*,*T* were of the pattern containing a T-shaped bore, so that the whole apparatus could be evacuated with the mercury pump or the pressure equalised throughout with that in the gas holder.

The required temperatures were obtained by immersing the bulb and a definite length of the tubing *ba* in a large test-tube containing aniline boiling under diminished pressure. By means of the water-pump and a spring pressure-regulator, it was found that the pressure could be kept constant to within a few millimetres. The readings of the single-tube gauge *G* give differences from observed barometric height, whence the temperatures are obtained from the known vapour-pressure curve for aniline. After evacuation, pure dry carbon dioxide was admitted from the gas-holder, all taps being open, and the levels in the two limbs *L* and *R* of the manometer consequently the same.

The taps *T*,*T* were then turned so that the limb *R* connected only with the gas holder, and the limb *L* only with the experimental bulb. The mass of gas in the bulb *B*, tubes *ba* and *aO*, and limb *L* to the mercury level, is therefore constant, whilst the pressure in the limb *R* is the same as that in the gas holder, and is found by reading, on the scale, the difference of level between the mercury in *R* and in the open tube *M*. By having a large mercury reservoir, this pressure is not sensibly affected by changes in atmospheric temperature. As a rule, the reservoir was fixed so that the excess pressure over the atmospheric was about 15 cm. of mercury.

The calibration of the apparatus was effected by removing the aniline jacket and immersing the bulb and tube *ba* in melting ice, water at 19°, and the vapours of boiling alcohol and boiling water successively. The mercury in the left limb of the manometer was adjusted to certain definite points of the scale between 0 and 40 cm., and the difference of height in the two limbs was read. The difference of pressure with change of volume was thus determined, the temperature of the exposed tubes and manometer being kept constant throughout at 19°.

From three such determinations, it is possible to calculate the volume of gas in the bulb and tube *ba*, and in the connecting tubes *aO* at 19° and 76 cm. pressure, and also the total volume of gas in the apparatus in terms of the volume of 1 cm. length of the manometer scale. The numbers obtained were:

Bulb and immersed tube	262·6 cm.	x
Connexions to zero point (0)......................	82·6 ,,	y
Total volume	364·0 ,,	M
Volume of 1 cm. of tube (by calibration) ...	0·029 c.c.	

The general formula used in calculation is:

$$x\frac{293}{T}+y+N=M\frac{76}{P},$$

where N is the required number of scale divisions.

The difference of the other observed readings from those calculated from the above data did not exceed 2 or 3 millimetres, showing that the manometer was of sufficiently even bore, also that no gas was evolved from the crystals on heating to 100°, and that no reaction had occurred.

The aniline vapour-bath was then replaced, and the temperature raised to successively higher temperatures.

In the succeeding absorption measurements, the mercury was always brought to the same level in the two tubes by raising or lowering the reservoir *M*, change of volume at constant pressure being thus measured, and the necessarily very small effects greatly magnified. The numbers so obtained therefore correspond with changes in volume of the gas in the heated portion of the apparatus due to thermal expansion and change of solubility, in terms of the volume of gas in unit length of the manometer scale, at constant known temperature and pressure. A thermometer suspended near the manometer stand enabled a small correction to be applied for changes in the laboratory temperature. The differences between the observed and calculated numbers, at various temperatures, then give the volumes of gas absorbed, in the same units.

Up to a temperature just below the first melting point, the readings agreed almost exactly with the volumes calculated for the successive temperatures. It is thus proved that, even with the very sensitive method employed, no change of gas absorption is observable between the temperatures of 0° and 131°. It seems impossible that, if any appreciable condensation of gas on the surface of the crystals occurs at low temperature, the same should persist over a wide range of temperature. It may therefore be taken as demonstrated that neither adsorption nor solution in the solid phase occurred, although the crystals consisted of small, very thin plates, uniformly well shaped, and recovering their original form completely after having been melted.

After the first melting point, absorption takes place, the observed volume diminishing considerably until equilibrium is reached. On further raising the temperature, normal thermal expansion again occurs, a minimum reading having thus been passed through. Expansion continues until the clearing point is reached. As soon as the isotropic liquid phase is reached, a second very well marked increase of absorption is observed, equilibrium being again reached at constant temperature. After this, expansion and decrease of solubility with rise of temperature proceed regularly.

On reversing the process by causing the aniline in the vapour jacket to boil at successively lower pressures, the corresponding maximum and minimum readings are repeated, although there is, of course, generally a considerable lag due to the very slow evolution of gas in passing from the isotropic to the liquid crystalline phase. The identical readings may, however, often be recovered, with sufficient patience, on the return journey.

The following table gives a typical experiment:

		Number of divisions.		
P.	*t*°.	Observed.	Calculated.	*D.*
92·4	100	10·0	10·0	0·0
92·4	131	24·3	24·2	0·1
90·6	143	38·6	39·4	0·8
—	158	16·6 (crystalline liquid)	45·0	28·8
—	160	17·1	45·9	28·8
—	161	13·0 (isotropic)	46·2	33·2

It was found, on comparing the melting and transition temperatures observed with those given by other experimenters, that the first melting point was too high, whilst the transition point was too low, the same numbers being obtained in the absence of carbon dioxide. It was therefore necessary to prepare and purify a fresh sample, that first used being presumably impure.

p-Nitrophenetole was recrystallised repeatedly from absolute alcohol, and then heated with sodium in absolute alcoholic solution. It was found that the best yields were obtained by boiling for only about a quarter of an hour with a reflux condenser, longer heating only increasing the amount of dark-coloured aldehydic resin. After cooling, the alcohol was decanted and the residue recrystallised some twenty times from absolute alcohol. The azoxy-compound is then obtained in fine, crystalline, pale yellow plates. The final yield is, however, small. The correct melting points, 138·5° and 168°, were then obtained. Two grams were taken, and the absorption experiments were carried out as before. The former results were completely confirmed, but, owing to the extension of the crystalline liquid phase, more readings could be obtained.

The following table gives the results of one series of measurements.

The equation from which the calculated values N were obtained was:

$$239{\cdot}4 \times \frac{293}{T} + 77 + N = 280{\cdot}4.$$

The constant pressure was 88·5 cm.

t°.	State.	*N* observed.	*N* calculated.	Difference.
134·0	(solid)	31·0	31·0	0
139·5		34·8	33·4	−1·4
145·5	(crystalline liquid)	17·7	35·8	18·1
149·0	,,	19·6	37·2	17·6
156·5	,,	22·5	40·1	17·6
160·0	,,	23·0	41·4	18·4
164·5	,,	24·2	43·0	18·8
166·5	,,	24·3	43·8	19·5
166·5	(liquid)	17·4	43·8	26·4
167·5	,,	18·0	44·2	26·2
169·0	,,	18·6	44·7	26·1

It is not to be expected that the liquid crystalline state would show the same impenetrability to gases as the rigid crystals, and we accordingly find considerable absorption in that phase. Also, it seems very probable that a certain amount of isotropic mother liquor may be present throughout the range of temperature in which the phase persists. This should not occur in the pure state, as the triple point is determined by a single temperature; the effect is probably due to the presence of the second component, namely, carbon dioxide, in solution. The melting point is decidedly less sharp than when dissolved gas is absent, and the temperature required is several degrees higher. Hulett (*Zeit. physikal. Chem.*, 1899, **28**, 639) has shown by means of transition-point curves that, whereas all crystalline liquids are completely miscible, other substances, whether of higher or lower melting points, are immiscible in this phase, and may even prevent its formation.

In connexion with experiments on surface-tensions of the two phases, Schenck has determined the density curve of this and other similar substances, and it appears that in the case of *p*-azoxyphenetole, there is decided expansion on passing to the isotropic phase. It is therefore necessary to determine how far this fact may account for the increase of absorption. The volumes of 2 grams were calculated from the densities at two temperatures, respectively above and below the transition point. The results are given below, together with the actual volumes of gas absorbed in 100 c.c. of liquid, taking the volume of each centimetre of the manometer tube as 0·03 c.c.:

$t°$.	N absorbed.	Volume. absorbed.	Volume of liquid.	Absorbed in 100 c.c.
145·5	18·1	0·54	1·824	29·6 c.c.
166·5	26·4	0·79	1·866	42·3 ,,

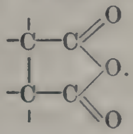
It is thus evident that the correction introduced is quite inappreciable on the scale of the present measurements, and the remarkable increase of absorption on changing from the crystalline to the isotropic phase, occurring in spite of the considerable rise of temperature, can only be attributed to the influence of the physical state of the solvent.

University College, London.

CLVII.—*The Rate of Hydration of Acid Anhydrides: Succinic, Methylsuccinic, Itaconic, Maleic, Citraconic, and Phthalic.*

By Albert Cherbury David Rivett and Nevil Vincent Sidgwick.

The present communication is an extension of the work on the rate of hydration of acetic anhydride (this vol., p. 732) to a series of anhydrides all containing the five-atom ring:



The method adopted was, as before, to measure at appropriate intervals of time the electrical conductivity of a changing solution of the anhydride in water, and to determine, over the same range of concentrations, the conductivity of aqueous solutions of the corresponding acid. As was pointed out (*loc. cit.*), the only condition in which the former measurements differ from the latter is in the presence of the unchanged anhydride, which may affect the conductivity by its influence on the viscosity, but will presumably have no other effect. In the only three cases where this condition need be considered, we have assumed that the conductivity is inversely proportional to the viscosity, and further, as was proved to be the case with acetic anhydride, that the viscosity of a solution of the anhydride is equal to that of an equivalent solution of the corresponding acid. Even if this is only approximately true, the error in the correction introduced will be slight.

In every instance we have redetermined the conductivities of the acids dealt with, because the accuracy of the velocity figures is greatly increased by making these measurements under as nearly as possible the same conditions as those obtaining in the velocity experiments. The same cells were therefore used for both purposes. The accuracy of the conductivity measurements is in all cases rather greater than is actually needed. The method adopted, of successive dilutions in the cell (every second dilution being checked by weight titration against 0·1 or 0·02N-baryta), is not the one which would be chosen for the highest accuracy, especially at the dilute end of a series. It is, however, unlikely that the error of measurement is anywhere greater than 1 part in 300, except perhaps in some of the most dilute solutions.

The slight modifications in the method of working necessary in particular cases will be mentioned under the respective anhydrides. Unless otherwise stated, the substances were obtained from Kahlbaum.

EXPERIMENTAL.

1. *Succinic Anhydride.*

The acid was purified by twice recrystallising from water, the anhydride by extraction with chloroform in a Soxhlet apparatus, and crystallisation from this solvent. It separates in long needles, melting at 119·5° (uncorr.). The cell used was about 160 c.c. in volume, with the electrodes sealed in; 120 c.c. of solution were always used. In the case of acetic anhydride, which is liquid, solution is so rapid that the time of mixing could be taken as the zero of the reaction, and the solution, after a brief period of shaking, could be poured into the cell, and the measurements begun. Succinic anhydride, being solid, dissolves much more slowly, and the following modification was necessary. A known weight of the anhydride was added to the right volume of water in a Jena flask (heated in the bath to 25°), and the stop-watch started. The mixture was violently shaken in the bath for from thirty-five to sixty seconds, and then rapidly drawn over by suction into the cell, passing on its way through a thick and closely packed filter of glass wool to retain undissolved particles. After shaking round in the cell, measurements were begun. The end-point was usually taken about two hours later. For the calculation it was necessary to take an initial time more definite than the beginning of solution. The first six or eight measurements were therefore plotted against the time, and a value of the concentration and time to be used as the starting point, and to be subtracted from all subsequent values, was obtained by interpolation. This time was usually about 140 seconds from the addition of the anhydride. The velocity constant is apparently quite independent both of the concentration of the anhydride and also of that of the acid, so that the calculation can be begun at any point.

As with acetic anhydride, the hydration follows the unimolecular law, that is, the rate is proportional to the concentration of the anhydride, that of the water being relatively constant at the dilutions used. But whereas with acetic anhydride a distinct though small variation of the constant with concentration was found to occur, no such variation was observed with succinic, nor with any of the cyclic anhydrides examined, with the possible exception of methylsuccinic.

Table I*a* gives the specific conductivity of solutions of succinic acid at 25°; I*b* the densities and viscosities, referred to water at

25° as unity; I*c* gives the full details of a typical velocity experiment, and I*d* the summary of all the experiments performed. In the last two tables, A is the difference between the concentration of the acid after the change is complete and that at time 0; it thus represents the concentration of the anhydride (in equivalent normality) at time 0; t is the time in seconds, and x the concentration of acid produced in time t. k is calculated from the equation:

$$k = 1/t.\log\frac{A}{A-x}.$$

Table I.

(a) Conductivity of Succinic Acid Solutions at 25°.

Normality.	Specific conductivity × 1000.	Normality.	Specific conductivity × 1000.
0·9813	1·955	0·06735	0·5534
0·8172	1·820	0·05622	0·5045
0·6806	1·687	0·04694	0·4597
0·5676	1·558	0·03911	0·4188
0·4730	1·438	0·03260	0·3809
0·3944	1·321	0·02721	0·3467
0·3285	1·214	0·02267	0·3156
0·2737	1·113	0·01987	0·2946
0·2279	1·019	0·01890	0·2869
0·2006	0·9580	0·01657	0·2682
0·1899	0·9320	0·01381	0·2435
0·1673	0·8756	0·009603	0·2007
0·1394	0·8006	0·006697	0·1656
0·1162	0·7298	0·004676	0·1364
0·09696	0·6661	0·003267	0·1120
0·08083	0·6077	0·002281	0·0918

(b) Density and Viscosity of Succinic Acid Solutions at 25°.

Normality.	Density.	Normality.	Viscosity.
0·9305	1·0165	0·9305	1·1102
0·5235	1·0093	0·6979	1·0815
0·2214	1·0040	0·2951	1·0344
0·09369	1·0017	0·1248	1·0144
0·03950	1·0007		

(*c*) *Experiment* 8. A = 0·1665.

t.	*x.*	*k.*	*t.*	*x.*	*k.*
8	0·00343	0·001153	257	0·0823	0·001152
29	0·01218	1139	279	0·0870	1151
37	0·01531	1139	317	0·0949	1156
59	0·02414	1156	342	0·1001	1167
80	0·03134	1134	373	0·1051	1162
90	0·03514	1146	419	0·1121	1159
104	0·03966	1137	462	0·1184	1167
131	0·0489	1153	523	0·1253	1160
145	0·0532	1153	589	0·1326	1174
161	0·0578	1150	676	0·1390	1157
181	0·0636	1155	971	0·1543	1169
213	0·0721	1157	1185	0·1593	1151
235	0·0771	1149		Mean	0·001154

(*d*) *Summary of Velocity Experiments.*

Expt.	*A.*	*k.*	Expt.	*A.*	*k.*
1	0·01113	0·001148	8	0·1665	0·001154
2	0·02042	1156	9	0·1873	1162
3	0·03920	1151	10	0·2746	1146
4	0·05261	1148	11	0·3145	1168
5	0·08093	1156	12*	0·1580	1165
6	0·10833	1152			
7	0·1373	1155		Mean ………	0·001155

* In this experiment, the anhydride was dissolved in water already containing acid of normality 0·3805.

2. *Methylsuccinic Anhydride.*

This anhydride was prepared from a pure sample of the acid by the method described by Perkin (Trans., 1888, **53**, 564). It consists in digesting the acid with acetyl chloride until action ceases, and fractionally distilling the product. The anhydride passed over within one degree, and was readily purified by redistillation. Like citraconic anhydride, it has a slight yellow colour after being distilled. It gave no trace of a precipitate with silver nitrate. The method of working was the same as with acetic anhydride. The cell had a volume of 100 c.c., and 80 c.c. of solution were always taken. The results are given in table II, in the same form as those for succinic anhydride in table I.

TABLE II.

(*a*) *Conductivity of Methylsuccinic Acid Solutions at* 25°.

Normality.	Specific conductivity × 1000.	Normality.	Specific conductivity × 1000.
0·4309	1·540	0·04425	0·4991
0·3233	1·352	0·03356	0·4304
0·2427	1·183	0·02539	0·3703
0·1821	1·029	0·01940	0·3189
0·1367	0·8935	0·01455	0·2738
0·1026	0·7745	0·01092	0·2352
0·07702	0·6702	0·00819	0·2015
0·05782	0·5787	0·00614	0·1726

(*b*) *Density and Viscosity.*

Normality.	Density.	Viscosity.
0·4885	1·0079	1·076
0·3456	1·0056	1·052
0·1638	1·0026	1·024

(*c*) *Summary of Velocity Experiments.*

Expt.	*A.*	*k.*	Expt.	*A.*	*k.*
13	0·03624	0·001658	18	0·1449	0·001599
14	0·05779	1666	19	0·1778	1570
15	0·06973	1636	20	0·2330	1580
16	0·09953	1602	21	0·2755	1573
17	0·1210	1597		Mean	0·001609

3. *Itaconic Anhydride.*

The acid and its anhydride were purified in the same way as succinic. Itaconic anhydride forms crystals which dissolve very rapidly in water. The stronger solutions were made in the way described under succinic anhydride, and the more dilute by simply placing an approximately known weight of the solid on a firm glass wool filter, and sucking the required amount of water through it directly into the cell. The initial point for the calculation was obtained by interpolation. The results are given in table III.

TABLE III.

(*a*) *Conductivity of Itaconic Acid at* 25°.

Normality.	Specific conductivity × 1000.
0·3870	1·946
0·2904	1·705
0·2179	1·487
0·1636	1·292
0·1227	1·120
0·09208	0·9686
0·06911	0·8366
0·05186	0·7208
0·03925	0·6207
0·02963	0·5338
0·02259	0·4587
0·01720	0·3934
0·01294	0·3375
0·009726	0·2883
0·007326	0·2462
0·005515	0·2099
0·004136	0·1785

(*b*) *Density and Viscosity.*

Normality.	Density.	Viscosity.
0·3433	1·0064	1·049
0·2689	1·0050	1·038
0·1484	1·0028	1·022

(*c*) *Summary of Velocity Constants.*

Expt.	*A.*	*k.*
23	0·01561	0·001283
24	0·02034	1320
25	0·02561	1305
26	0·04669	1288
27	0·07185	1273
28	0·07955	1264
29	0·09587	1303
30	0·1371	1311
31	0·1793	1311
32	0·2269	1283
	Mean	0·001294

4. *Maleic Anhydride.*

The anhydride was purified by sublimation in a vacuum, and the acid solutions required were made up directly from this. The substance dissolves fairly rapidly, but is very quickly hydrated; as a rule, the change was found to be practically complete about two and a-half minutes after the making of the solution was begun. Hence the measurements must be made as quickly as possible, and the accuracy is reduced.

The solutions were all obtained by sucking water into the cell over a layer of anhydride on a glass wool filter. It was, of course, impossible to obtain strong solutions, and no correction for viscosity was necessary. An approximate initial time was taken when half the water had been drawn into the cell, but for the calculation a zero time, usually about forty seconds later than this, was arrived at by interpolation. The results are given in table IV.

TABLE IV.

(*a*) *Conductivity of Maleic Acid.*

Normality.	Specific conductivity × 1000.	Normality.	Specific conductivity × 1000.
0·06031	5·503	0·009386	1·366
0·04525	4·515	0·007055	1·075
0·03930	4·098	0·005334	0·8396
0·03394	3·687	0·004021	0·6521
0·02949	3·330	0·003042	0·5032
0·02213	2·695	0·002304	0·3865
0·01664	2·186	0·001728	0·2954
0·01250	1·724	0·001296	0·2252

(*b*) *Experiment* 37. A = 0·00353.

t.	*x.*	*k.*	*t.*	*x.*	*k.*
6	0·00054	0·0120	57	0·00277	0·0117
9	0·00082	116	66	0·00293	117
14	0·00105	110	76	0·00307	116
18	0·00133	114	87	0·00317	114
23	0·00160	114	99	0·00326	113
28	0·00189	119	114	0·00334	111
35	0·00217	118	153	0·00347	116
42	0·00235	113			
49	0·00259	117		Mean	0·0115

(*c*) *Summary of Velocity Constants.*

Expt.	*A.*	*k.*	Expt.	*A.*	*k.*
33	0·000985	0·0114	38	0·00649	0·0106
34	0·001771	122	39	0·01094	110
35	0·001537	113	40	0·01961	118
36	0·002999	119			
37	0·00353	115		Mean	0·0115

5. *Citraconic Anhydride.*

The anhydride was purified by distillation. It has a slight yellow colour. The acid solutions were made up from this. The method of work was the same as with acetic and methylsuccinic anhydrides. The range of concentration employed was much the same as with maleic anhydride, and no correction for viscosity was necessary. The results are given in table V.

TABLE V.

(*a*) *Conductivity of Citraconic Acid.*

Normality.	Specific conductivity × 1000.	Normality.	Specific conductivity × 1000.
0·10268	4·476	0·01376	1·275
0·07683	3·787	0·01034	1·045
0·05763	3·189	0·007775	0·8506
0·04326	2·679	0·005818	0·6882
0·03245	2·240	0·004358	0·5527
0·02436	1·868	0·003269	0·4405
0·01833	1·547	0·002452	0·3485

(*b*) *Summary of Velocities.*

Expt.	*A.*	*k.*	Expt.	*A.*	*k.*
41	0·004305	0·00761	47	0·05005	0·00761
42	0·006634	771	48	0·06100	776
43	0·01407	769	49	0·07504	758
44	0·02074	777	50	0·08287	761
45	0·03093	758			
46	0·03682	761		Mean	0·00765

6. *Phthalic Anhydride.*

The acid was recrystallised twice from water, and the anhydride twice from xylene. The method of working, and of determining the initial point for the calculation, was that adopted for succinic anhydride, but owing to the small solubility of both acid and anhydride, the concentrations examined are all low, although the relative range is considerable. No viscosity correction is necessary. Table VI gives the results obtained.

TABLE VI.

(*a*) *Conductivity of Phthalic Acid at 25°.*

Normality.	Specific conductivity × 1000.	Normality.	Specific conductivity × 1000.
0·05506	1·954	0·008946	0·6656
0·04587	1·763	0·007474	0·5917
0·03819	1·592	0·006228	0·5268
0·03181	1·437	0·004955	0·4427
0·02652	1·293	0·004149	0·3913
0·02210	1·159	0·003486	0·3460
0·01843	1·042	0·002427	0·2661
0·01539	0·934	0·001686	0·2037
0·01283	0·8358	0·001188	0·1530
0·01071	0·7469	0·000825	0·1145

(*b*) *Summary of Velocities.*

Expt.	*A.*	*k.*	Expt.	*A.*	*k.*
51	0·000650	0·00470	56	0·002145	0·00455
52	0·001048	470	57	0·00348	454
53	0·001320	466	58*	0·00382	454
54	0·001855	469			
55	0·002120	466		Mean	0·00461

* In this experiment, the anhydride was dissolved in water already containing acid of normality 0·02754.

Discussion of Results.

The mean velocity constants for the hydration of this series of anhydrides are given in the following table, together with the dissociation constants of the corresponding acids.

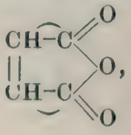
	Velocity constant.		Dissociation constant of acid.	
Anhydride.	Absolute.	Relative.	Absolute.	Relative.
[Acetic	0·001148	0·99]	—	—
Succinic...........................	0·001155	**1·00**	0·0066	**1·00**
Methylsuccinic....................	0·001609	1·39	0·0086	1·30
Itaconic (methylenesuccinic)	0·001294	1·12	0·012	1·82
Maleic	0·0115	9·96	1·2	182·0
Citraconic (methylmaleic) ...	0·00765	6·62	0·34	51·5
Phthalic	0·00461	3·99	0·121	18·3

The mean value for acetic anhydride, over the range of concentrations covered by the succinic experiments, has been added for comparison; the individual values vary from 0·001192 to 0·001075.

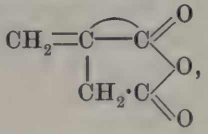
It is to be noticed, in the first place, that in none of the cases examined is there any evidence of a catalytic influence of hydrogen ion; and it seems clear that the mechanism of the hydration of an acid anhydride is quite different from that of the hydrolysis of an ester or an amide.

Further, it is remarkable that in the cyclic anhydrides no dependence of the velocity constant on the concentration, such as was observed in acetic anhydride, was detected, except possibly in methylsuccinic anhydride, although even here the effect was very slight.

The close agreement between the constants for acetic and succinic anhydrides affords a good illustration of Baeyer's strain theory: the ring of four carbon atoms and one oxygen having practically no strain, and resembling most nearly an open-chain compound. In maleic anhydride, where there is a full double link, and indeed, according to Thiele, two conjugate links as well,



the constant is increased ten times; in phthalic there is the peculiar benzene link, which, whatever may be its precise nature, is intermediate in character between a single and a double link, and this increases the constant four times. In itaconic there is, on Thiele's theory, a conjugate link in the ring,



and this causes a slight rise in the constant.

The influence of a methyl group, however, is quite anomalous. Its introduction lowers the constant of maleic anhydride by a third, while it raises that of succinic by about two-fifths. It is noteworthy that the effect of the methyl on the dissociation constants of the corresponding acids is likewise in the opposite direction in these two cases; in fact, in general the order of the dissociation constants of these acids is the same as that of the hydration constants of their anhydrides, except in the case of methylsuccinic and itaconic, where, moreover, the differences are not large. It is evident that with these substances the same changes of structure, and especially the introduction of double links, tend to increase both of these constants, though how far this regularity may be general, and how far stereochemical influences (which would presumably affect the hydration rather than the ionisation, and may possibly account for the exceptional position of methylsuccinic anhydride) may come into play, is a question which cannot be discussed until a wider range of anhydrides has been examined.

The considerable diminution of the hydration constant of maleic anhydride caused by the introduction of a methyl group is of interest in view of the singular behaviour of dimethylmaleic anhydride. This anhydride is formed spontaneously from the acid, which, in fact, cannot be isolated. It has been shown by Walden (*Zeitsch. physikal. Chem.*, 1891, **8**, 498) that an aqueous solution of dimethylmaleic anhydride (and similarly of methylethylmaleic anhydride) can only contain a comparatively small amount of the corresponding acid, since conductivity measurements indicate an abnormally low dissociation constant, and the solution can only be slowly titrated with alkali. The arguments by which Walden seeks to prove that the rest is not present as anhydride are of no great force, and we may assume that with these two substances the hydration is reversible, and that at equilibrium there is present a large proportion of anhydride and a small proportion of acid. It is conceivable that the reaction may also be reversible with some of the substances which we have examined. We did not observe in any case a difficulty in the titrations, but this might well be imperceptible if the amount of anhydride were small. If the reverse action (acid → anhydride) is also unimolecular, and its velocity is k_1 (that of the direct action being k), it can easily be shown that the substance will give an apparent dissociation constant independent of the dilution, but that this will be less than the real dissociation constant in the ratio $1:(1+k_1/k)$. In the same way, the apparent hydration constant will also be independent of the dilution, but instead of being, as we have assumed, the true hydration constant k, will be the sum of the two, $k+k_1$. Thus, the effect of the reverse action being appreciable would be to make the apparent value of the dissociation constant too low (as it does with dimethylmaleic anhydride), and that of the hydration constant too high. It therefore could not possibly explain the anomalous effect of the methyl group, which influences both constants in the same way. In any case, the amount of the reverse action with the bodies which we have examined must be small, or it would have shown itself in the absence of a sharp end-point to the titrations.

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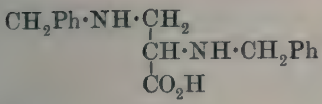
CLVIII.—*$\alpha\beta$-Dibenzylaminopropionic Acid and* 1 : 7-*Dibenzyltetrahydrouric Acid.*

By EDWARD PERCY FRANKLAND.

THE present paper describes the synthesis of 1 : 7-dibenzyltetrahydrouric acid (IV) on the lines followed by the author in the recent synthesis of tetrahydrouric acid from $\alpha\beta$-diaminopropionic acid (this vol., p. 1316), namely, by the addition of cyanic acid to the substituted amino-groups, followed by condensation by means of hydrochloric acid.

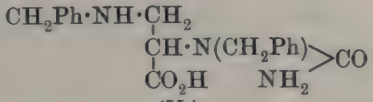
The new dibenzyltetrahydrouric acid is of interest in view of the fact that Tafel, the discoverer of tetrahydrouric acid, was unable to produce substituted tetrahydrouric acids by the electrolytic reduction of the methyluric acids, and that consequently substances of this class appear to be accessible only from the synthetic side.

Starting from the hitherto unknown $\alpha\beta$-dibenzylaminopropionic acid (I), it was found possible to isolate several intermediate compounds before dibenzyltetrahydrouric acid (IV) was produced,



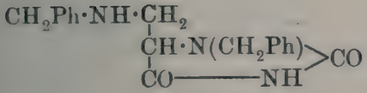
$$\begin{array}{ll} CH_2Ph\cdot NH\cdot CH_2 & \\ & CH\cdot NH\cdot CH_2Ph \\ & CO_2H \end{array}$$

(I.)



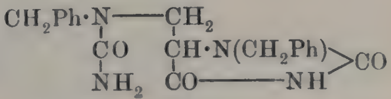
$$\begin{array}{ll} CH_2Ph\cdot NH\cdot CH_2 & \\ & \left.\begin{array}{l} CH\cdot N(CH_2Ph) \\ CO_2H \quad NH_2 \end{array}\right> CO \end{array}$$

(II.)



$$\begin{array}{ll} CH_2Ph\cdot NH\cdot CH_2 & \\ & \left.\begin{array}{l} CH\cdot N(CH_2Ph) \\ CO\text{———}NH \end{array}\right> CO \end{array}$$

(III.)



$$\begin{array}{ll} CH_2Ph\cdot N\text{——} & CH_2 \\ \quad CO & \left.\begin{array}{l} CH\cdot N(CH_2Ph) \\ CO\text{———}NH \end{array}\right> CO \\ \quad NH_2 & \end{array}$$

(IV.)

whereas in the case of the synthesis of tetrahydrouric acid from $\alpha\beta$-diaminopropionic acid, no such analogous substances could be obtained, serving to illustrate the course of the reaction.

In the present case, the difference in chemical behaviour between the α- and the β-benzylamino-groups is strikingly shown, only one group reacting with potassium cyanate even in presence of excess of the reagent. This fact suggests that one or other of the imino-groups is shielded either by steric obstruction or by combination with the free carboxyl group, forming an internal salt. Judging from the action of nitrous acid on the $\alpha\beta$-diamino-acid, in which case the β-group appears to be indifferent to the reagent, in the present instance it seems most likely that the cyanic acid attaches itself to the α-group. Thus, for the compounds described below, it has been decided to omit the alternative formulæ based on the primary addition of cyanic acid to the β-benzylamino-group. Further investigations are, however, being carried out with the view of testing the above hypothesis.

$\alpha\beta$-Dibenzylaminopropionic acid was prepared by the action of benzylamine on $\alpha\beta$-dibromopropionic acid in chloroform solution; it is capable of uniting with two molecules of hydrochloric acid to form a salt. As was shown by Tafel and Frankland (*Ber.*, 1909, **42**, 3138) in the case of β-amino-α-methylaminopropionic acid and $\alpha\beta$-dimethylaminopropionic acid dihydrochlorides, hydrogen chloride is readily eliminated in aqueous solution, probably with formation of an internal salt between one of the benzylamino-groups and the carboxyl.

When a hot aqueous solution of dibenzylaminopropionic acid was treated with potassium cyanate (2 molecules) and hydrochloric acid, it yielded *β-benzylamino-α-benzylcarbamidopropionic acid* (II), which, on warming with 25 per cent. hydrochloric acid, was converted into *β-benzyl-γ-benzylaminomethylhydantoin hydrochloride.* The principal product of the action of potassium cyanate on this substance was the free *β-benzyl-γ-benzylaminomethylhydantoin* (III), but by the long-continued action of potassium cyanate and hydrochloric acid in aqueous methyl alcohol, this compound could be made to yield the urea derivative, 1 : 7-*dibenzyltetrahydrouric acid* (IV).

EXPERIMENTAL.

αβ-Dibenzylaminopropionic Acid.

7·5 Grams of $\alpha\beta$-dibromopropionic acid were dissolved in a solution of 14 grams of benzylamine in chloroform, and the mixture was heated to boiling under reflux. After about fifteen minutes, a crystalline precipitate was deposited, which, after being collected, washed with chloroform, and dried, weighed 4·6 grams. This substance proved to be benzylamine hydrobromide (m. p. 215° after recrystallisation from water). The reaction mixture was heated on the water-bath until no further precipitation occurred; the chloroform was then distilled off, and the brown, oily residue heated in the water-bath for half an hour longer. It was then extracted with ether, and the residue dissolved in a mixture of boiling ethyl and methyl alcohol; the solution was concentrated and precipitated with ether. The precipitate of dibenzylaminopropionic acid was washed with alcohol and ether, recrystallised from boiling water, washed again with alcohol and ether, and, after drying in the steam-oven, weighed 3·2 grams. By concentrating the mother liquors (which contained a quantity of benzylamine hydrobromide), 0·5 gram of crude dibenzylaminopropionic acid was obtained.

The substance dissolved fairly easily in boiling water, and separated from the cooled solution in large, crystalline aggregates; it was very sparingly soluble in cold water (1 : 898 at 14°), the solution showing an alkaline reaction to litmus, readily soluble in warm methyl alcohol, sparingly so in absolute ethyl alcohol, and almost insoluble in ether. It formed rhomboidal plates from methyl alcohol, melting and decomposing at 181—184°:

0·2978 gave 0·7791 CO_2 and 0·1920 H_2O. C = 71·35; H = 7·19.
0·1274 ,, 11·4 c.c. N_2 at 18° and 739·7 mm. N = 10·05.
$C_{17}H_{20}O_2N_2$ requires C = 71·83; H = 7·04; N = 9·86 per cent.

A portion of the dibenzylaminopropionic acid was dissolved in warm aqueous hydrochloric acid. After concentration on the water-bath the solution deposited, on cooling, a white, crystalline substance, which was collected, washed with dilute hydrochloric acid, alcohol, and ether, and was dried in a vacuum desiccator. The substance decomposed with blackening and evolution of gas at 187°. It was soluble in water, the solution showing an acid reaction to litmus, soluble in alcohol, and insoluble in ether. A hydrochloric acid estimation showed this compound to be *αβ-dibenzylaminopropionic acid dihydrochloride*:

0·1987 gave 0·1595 AgCl. Cl=19·86.
$C_{17}H_{20}O_2N_2,2HCl$ requires Cl=19·89 per cent.

A specimen recrystallised from water gave Cl=17·09, showing that solutions of the dihydrochloride are stable only in presence of an excess of hydrochloric acid.

1 : 7-*Dibenzyltetrahydrouric Acid.*

Three grams of dibenzylaminopropionic acid were dissolved in hot water and treated with 2·4 grams of potassium cyanate. After cooling, 3·6 grams of concentrated hydrochloric acid were added to the solution, giving rise to a slight effervescence. The solution was then concentrated on the water-bath, and after some time a crystalline precipitate was slowly deposited in white flakes. It was collected, washed with water, then with a little absolute alcohol, and finally with ether. After drying in the steam-oven, it weighed 2·4 grams. It crystallises from alcohol in spherical aggregates of small prisms, melting and decomposing at 200—201°, which are very sparingly soluble in water, soluble in alcohol, and insoluble in ether:

0·0450 gave 54·79 c.c. CO_2 at N.T.P. and 4·75 c.c. N_2 at N.T.P.*
C=65·47; N=13·24.
0·0821 gave 9·5 c.c. N_2 at 20° and 752·8 mm. N=13·11.
$C_{18}H_{21}O_3N_3$ requires C=66·05; N=12·84 per cent.

β-Benzylamino-α-benzylcarbamidopropionic acid (II) was also obtained by treating an aqueous solution of dibenzylaminopropionic acid dihydrochloride with potassium cyanate, but a less pure product was obtained, and the yield was considerably smaller than that furnished by the method described above. A solution of 2 grams of this compound in about 20 c.c. of 25 per cent. hydrochloric acid was heated on the water-bath, whereupon a crystalline precipitate separated out, which was collected, washed with concentrated hydrochloric acid, then with a little absolute alcohol, and finally with ether. After drying in the steam-oven, it weighed 1·95 grams. The mother liquor yielded a further quantity of the substance (0·15 gram).

β-Benzyl-γ-benzylaminomethylhydantoin hydrochloride crystallises in stellate groupings of prisms, melting without noticeable decomposition at 224°. It is sparingly soluble in water, the solution showing an acid reaction to litmus, more easily soluble in methyl than in ethyl alcohol, and insoluble in ether:

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* Carbon and nitrogen combustion in a vacuum.

0·1331 gave 14·7 c.c. N_2 at 21° and 742 mm. N = 12·27.
0·2779 „ 0·1166 AgCl. Cl = 10·38.
$C_{18}H_{19}O_2N_3,HCl$ requires N = 12·16; Cl = 10·27 per cent.

1·5 Grams of this hydantoin hydrochloride were dissolved in aqueous methyl alcohol, and treated with a strong aqueous solution of 0·45 gram of potassium cyanate. An oily precipitate was deposited, which after some time set to a crystalline mass. This was collected, washed with alcohol and ether, and dried in the steam-oven. A further quantity was isolated from the mother liquor and washings, the total weight obtained being 1·33 grams. Melting point 178—180°.

The substance was boiled with a mixture of ethyl and methyl alcohol, when a part (0·3 gram) remained undissolved and melted and decomposed at 195—196°.

The solution, on concentration, yielded a crystalline substance (0·25 gram), which was collected and washed with alcohol and ether. After two recrystallisations from methyl alcohol and drying in a vacuum desiccator, it melted at 112—115°.

β-Benzyl-γ-benzylaminomethylhydantoin (III) forms long, needle-shaped crystals, sparingly soluble in water, but soluble in alcohol or ether. For analysis, it was recrystallised from ether to remove the last traces of a substance of high melting point:

0·1292 gave 15·9 c.c. N_2 at 20° and 739·5 mm. N = 13·69.
$C_{18}H_{19}O_2N_3$ requires N = 13·59 per cent.

Treatment with hydrochloric acid yielded the hydantoin hydrochloride described above.

In a second experiment 2·5 grams of the hydrochloride were treated with a warm solution of 0·4 gram of potassium hydroxide, whereby a colourless oil was deposited, solidifying on cooling. This was doubtless the free base described above. A mixture of ethyl and methyl alcohol was added, and the solution was heated until the precipitate had redissolved. A methyl-alcoholic solution of 0·7 gram of potassium cyanate was then added. On cooling, a precipitate of long needles appeared, which was evidently the unattacked hydantoin. The mixture was consequently warmed again, and a second portion of 0·7 gram of potassium cyanate added, followed by 1·9 grams of concentrated hydrochloric acid. On cooling, a gummy substance separated out, with a mass of fine, needle-shaped crystals. On heating the mixture, the crystals redissolved in the solution, which was poured off from the gum, and the latter extracted with ether. The ethereal extract was evaporated, and the residue returned to the mother liquor; the undissolved portion corresponded with the substance of high melting point obtained in the first experiment and melted and decomposed at 189—190°.

This process was repeated five times, 0·7 gram of potassium cyanate being added on each occasion, the solution boiled for a time, then cooled, and treated with 0·9—1·0 gram of concentrated hydrochloric acid. The resulting precipitate was extracted with ether as above described, and the portions insoluble in ether were collected and tested separately. The melting points obtained varied from 173° to 179°. The total yield of substance insoluble in ether amounted to 1·8 grams.

This product was boiled with a large volume of methyl alcohol under a reflux condenser until all but a small residue had dissolved. The solution was then filtered hot and concentrated to a small bulk. A pure white substance crystallised out, which was collected, washed with ether, and dried in the steam-oven. It formed aggregates of small, prismatic crystals, melting at 177—178°, which were very sparingly soluble in water, sparingly soluble in methyl alcohol, and insoluble in ether.

The results of analysis agreed with the composition of the expected 1 : 7-*dibenzyltetrahydrouric acid* (IV):

0·0490 gave 58·98 c.c. CO_2 at N.T.P. and 6·23 c.c. N_2 at N.T.P.*
$C=64·71$; $N=15·95$.
0·0996 gave 14·3 c.c. N_2 at 23° and 747 mm. $N=15·90$.
$C_{19}H_{20}O_3N_4$ requires $C=64·77$; $N=15·91$ per cent.

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CLXXIX.—*The Colour and Constitution of Diazonium Salts. Part II. Diazo-derivatives of* as-*Benzoylethyl*-1 : 4-*naphthylenediamine.*

By GILBERT T. MORGAN and EDWARD GORDON COUZENS, B.Sc., A.R.C.S.

IN a previous communication on diazonium salts it was shown that benzoyl-1 : 4-naphthylenediamine (I) gives rise to a series of remarkably stable diazonium derivatives (II), which are all distinctly coloured, usually in various shades of yellow (Morgan and Wootton, Trans., 1907, **91**, 1311):

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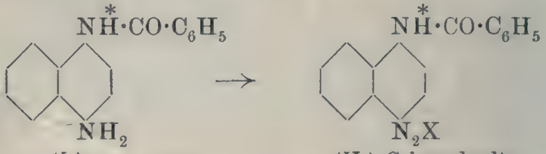
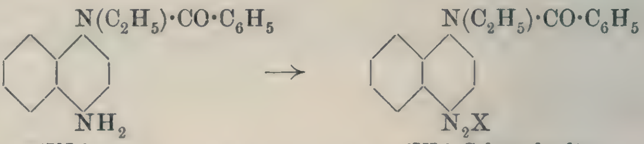
* Carbon and nitrogen combustion in a vacuum.



(I.) (II.) Coloured salts.

Inasmuch as colour and stability are not generally associated in diazonium salts (Hantzsch, *Ber.*, 1900, **33**, 2183; 1901, **34**, 4168), it was suggested that the concurrence of these properties in the diazo-derivatives of benzoyl-1:4-naphthylenediamine indicated a departure from the ordinary diazonium configuration. This view of the constitution of these salts is quite justifiable, because benzoyl-1:4-naphthylenediamine certainly contains one labile hydrogen atom (*) which might migrate to the diazonium complex.

With the object of ascertaining whether this assumed migration of hydrogen is the cause of the stability and intense colour of benzoyl-4-aminonaphthalene-1-diazonium chloride and its analogues (II), the base as-*benzoylethyl*-1:4-*naphthylenediamine* (III) and its diazonium salts (IV) were prepared and examined from this point of view:

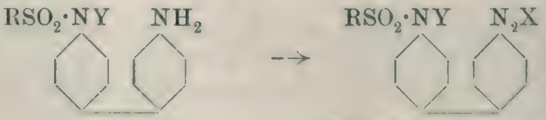


(III.) (IV.) Coloured salts.

These experiments showed that even when the labile hydrogen of benzoyl-1:4-naphthylenediamine is replaced by ethyl, the diazonium salts (IV) of the new base (III) are fairly stable, and retain their intense yellow colour even in dilute aqueous solution.

The observations recorded in the present communication should be compared with the evidence already obtained from a comparative study of similarly constituted salts in the diphenyl and benzene series.

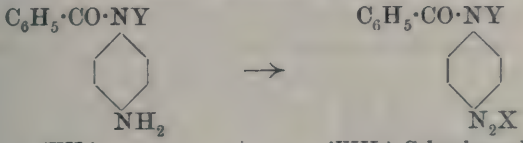
In the former series, the bases having the general formula (V) give rise to stable coloured diazonium salts (VI), whether the symbol Y represents a hydrogen atom or an alkyl group:



(V.) (VI.) Yellow and orange salts.

A slight colour difference is noticeable in this series, the diazonium salts (VI), when Y is an alkyl group, being distinctly paler in tint than those in which Y is a hydrogen atom (Trans., 1907, **91**, 1505; 1908, **93**, 614).

In the latter series both benzoyl-*p*-phenylenediamine and its *as*-alkyl derivatives (VII) give rise to colourless diazonium salts (VIII) possessed of considerable stability (Trans., 1909, **95**, 1319):



(VII.) (VIII.) Colourless salts.

In the benzene series, these diazonium salts are uniformly colourless, in the diphenyl series they are coloured to a varying extent, whilst in the naphthalene series the colour is approximately the same whether the salt is derived from benzoyl-1 : 4-naphthylenediamine or its ethyl derivative.

This comparative study of a series of fairly stable diazonium salts containing benzene, diphenyl, and naphthalene nuclei leads to the conclusion that the appearance of colour in this class of diazo-derivatives is due, not to any change in the constitution of the diazonium group, but to a gradual increase in the complexity of the aromatic nucleus associated with the diazonium radicle.

EXPERIMENTAL.

as-*Benzoylethyl*-1 : 4-*naphthylenediamine* (III).

4-Chloro-α-nitronaphthalene (20 grams) was heated in a steel tube, closed with steel caps and leaden washers, for six hours with 80 c.c. of alcohol and 50 c.c. of 33 per cent. alcoholic ethylamine. The product, 4-nitroethyl-α-naphthylamine, was separated from unchanged chloro-compound by extraction with light petroleum, the yield being about 50 per cent.

Benzoyl-4-nitroethyl-α-naphthylamine,

$$NO_2\cdot C_{10}H_6\cdot N(C_2H_5)\cdot CO\cdot C_6H_5,$$

prepared by heating 5 grams of the preceding compound in dry toluene with a slight excess of benzoyl chloride, crystallised from benzene or alcohol in pale yellow prisms, and melted at 121° (yield, 80 per cent):

0·2337 gave 18·3 c.c. N_2 at 21° and 766 mm. N = 8·89.

$C_{19}H_{16}O_3N_2$ requires N = 8·75 per cent.

The nitro-compound (4 grams) was dissolved in 50 c.c. of alcohol, and reduced with 3·5 grams of tin and 12 c.c. of concentrated hydrochloric acid. After boiling for about thirty minutes, the cooled solution yielded a pink, crystalline precipitate, probably a stannichloride. This product, when decomposed with warm aqueous sodium hydroxide and extracted with benzene, furnished a base which, after recrystallisation from the same solvent, separated in small, yellowish-white needles, and melted at 205°:

0·2817 gave 23·8 c.c. N_2 at 19° and 762 mm. N = 9·74.

$C_{19}H_{18}ON_2$ requires N = 9·65 per cent.

Benzoylethyl-4-aminonaphthalene-1-diazonium Sulphate. — The foregoing base (0·5 gram) was suspended in 2 c.c. of glacial acetic acid, and treated with an equal weight of nitrosyl sulphate. A yellow coloration developed immediately and deepened rapidly, until after about thirty minutes a drop of the solution diluted with water no longer gave a precipitate of the unchanged base. In order to complete the diazotisation, it was sometimes found necessary to warm the acetic acid solution, but this procedure should be avoided so far as possible.

The solution of diazonium sulphate was then poured into six or seven times its volume of warm dry ether, when the diazonium salt was precipitated as a yellow oil, which solidified only after treatment with alcohol. Addition of more alcohol and ether to the supernatant mother liquor produced a further precipitation of crystalline diazonium salt, the total yield being practically quantitative. The following analyses were made on different specimens of the diazonium sulphate:

0·1330 gave 10·6 c.c. N_2 at 15° and 765 mm. N = 9·40.
0·2667 „ 22·3 c.c. N_2 „ 19° „ 759 mm. N = 9·60.
0·3151 „ 0·1710 $BaSO_4$. S = 7·47.

$C_{21}H_{23}O_6N_3S$ requires N = 9·44; S = 7·19 per cent.

These numbers correspond with the formula

$$N(C_2H_5)(CO{\cdot}C_6H_5){\cdot}C_{10}H_6{\cdot}N_2{\cdot}HSO_4,C_2H_5{\cdot}OH.$$

This sulphate separates in fine, yellow leaflets, softening at 87°, and decomposing with effervescence at 96°; it dissolves readily in water to a clear yellow solution, which is acid to litmus, and gives at once a precipitate of barium sulphate with barium chloride. The diazonium salt couples immediately with alkaline β-naphthol. Although stable in the dark, this salt undergoes decomposition in the light; it then darkens, becomes tarry, and evolves an odour of ethyl benzoate.

Larger crystals of the salt can be obtained by dissolving it in alcohol and then adding the minimum amount of ether to induce crystallisation; this preparation contains 9·16 per cent. of nitrogen.

The diazotisation with nitrosyl sulphate was tried in alcoholic solution, but a less stable product was obtained, which did not give a precipitate with aqueous barium chloride. In this case a diazonium ethylsulphate was probably produced.

Benzoylethyl-4-aminonaphthalene-1-diazonium perchlorate,

$$N(C_2H_5)(CO\cdot C_6H_5)\cdot C_{10}H_6\cdot N_2\cdot ClO_4,$$

was obtained as a bright yellow, crystalline precipitate on mixing cold aqueous solutions of the foregoing sulphate and potassium perchlorate, the yield being about 50 per cent. of the calculated amount:

0·1342 gave 11·2 c.c. N_2 at 17° and 771 mm. N = 9·82.

$C_{19}H_{16}O_5N_3Cl$ requires N = 10·45 per cent.

The perchlorate is decomposed by warm water, yielding a viscid product; cold water hydrolyses it with the formation of a yellow, crystalline substance (compare p. 1696); it detonates with difficulty on percussion, and explodes at about 154°. The coupling with alcoholic β-naphthol takes place in the presence of a mild alkali, such as sodium carbonate or calcium hydroxide, but is inhibited by sodium or potassium hydroxide.

Benzoylethyl-4-aminonaphthalene-1-diazonium stannichloride,

$$N(C_2H_5)(CO\cdot C_6H_5)\cdot C_{10}H_6\cdot N_2\cdot HSnCl_6,$$

separated as a bulky, yellow precipitate on mixing cold aqueous solutions of the diazonium sulphate or chloride and ammonium stannichloride:

0·1048 gave 6·5 c.c. N_2 at 20° and 754 mm. N = 7·04.

$C_{19}H_{17}ON_3Cl_6Sn$ requires N = 6·67 per cent.

The stannichloride couples directly with alkaline β-naphthol, and decomposes at 154°.

Benzoylethyl-4-aminonaphthalene-1-diazonium chloride was prepared by suspending *as*-benzoylethyl-1 : 4-naphthylenediamine in glacial acetic acid, and passing in dry hydrogen chloride until the base had dissolved to a clear pink solution. On adding successively amyl nitrite and warm dry ether, a greenish-yellow, crystalline precipitate was obtained, which, although not pure enough for analysis, gave all the reactions of the diazonium chloride. The product dissolved in cold water to a clear yellow solution; it coupled directly with alkaline β-naphthol, and decomposed at about 100°. The corresponding *diazo-cyanide*, $N(C_2H_5)(CO\cdot C_6H_5)\cdot C_{10}H_6\cdot N_2\cdot CN$, prepared by mixing dilute alcoholic solutions of the diazonium chloride or sulphate and potassium cyanide at −10°, separated at once as a dark red precipitate, which, when dry, contained 16·31 per cent. of nitrogen, the calculated proportion being 17·07. The cyanide thus produced does not couple with alkaline β-naphthol either before or after treatment with cold concentrated sulphuric acid. The *diazonium molybdate* and *diazonium tungstate* were obtained as unstable, yellow precipitates, coupling directly with alkaline β-naphthol, by mixing concentrated aqueous solutions of the diazonium sulphate and sodium molybdate and tungstate respectively.

The Decomposition Products of Benzoylethyl-4-aminonaphthalene-1-diazonium Salts.

1. *Hydrolysis.*—The diazonium salts from *as*-benzoylethyl-1 : 4-naphthylenediamine, if treated with excess of cold water or with aqueous solutions of the alkali salts of weak acids, such as sodium acetate, undergo a definite hydrolytic decomposition with the formation of a crystalline, yellow substance, which dissolves readily in concentrated hydrochloric acid, and separates unchanged in well-defined, pale yellow, felted leaflets when the acid solution is diluted with cold water. This compound, which melts at 140°, loses in weight when kept in a desiccator over phosphoric oxide. This loss is due to the removal of water, for on exposure to a moist atmosphere the desiccated product takes up water until the original weight is regained. The following analyses were made on the dried product:

0·1826 gave 0·4788 CO_2 and 0·0911 H_2O. $C=71·49$; $H=5·54$.
0·2077 ,, 23·8 c.c. N_2 at 20° and 764 mm. $N=13·23$.
0·1321 absorbed 0·0074 H_2O. $H_2O=5·59$.
$C_{19}H_{17}O_2N_3$ requires $C=71·47$; $H=5·34$; $N=13·16$; and H_2O added requires 5·40 per cent.

These numbers correspond with the formula for a nitrosoamine, $NO\cdot NH\cdot C_{10}H_6\cdot N(C_2H_5)\cdot CO\cdot C_6H_5$, which becomes hydrated by the NO group, changing to $N(OH)_2$. Its solution in concentrated hydrochloric acid does not contain any regenerated diazonium salt, as no coupling occurs with alkaline β-naphthol. The yellow alcoholic solution of this basic compound is decolorised by zinc dust and ammonium chloride, yielding a reduction product melting at 207°. Owing to the small amount of available material, the study of these substances was not carried further.

2. *Action of Ammonia.*—The diazonium salts of *as*-benzoylethyl-1 : 4-naphthylenediamine, when treated with aqueous ammonia, furnish a brown product, which decomposes at 108°, and does not couple with alkaline β-naphthol:

0·1513 gave 15·5 c.c. N_2 at 19·5° and 748·5 mm. $N=11·63$.
$C_{38}H_{33}O_2N_5$ requires $N=11·80$ per cent.

This result, which agrees with the formula for a diazoamine, $N(C_2H_5)(CO\cdot C_6H_5)\cdot C_{10}H_6\cdot N_2\cdot NH\cdot C_{10}H_6\cdot N(C_2H_5)(CO\cdot C_6H_5)$, is confirmed by the action of cold concentrated hydrochloric acid. This acid slowly dissolves the substance, forming a solution which now couples with alkaline β-naphthol.

3. *Action of Sodium Azide.*—Even in cooled solutions it was found impossible to obtain the yellow diazonium azide of *as*-benzoylethyl-1 : 4-naphthylenediamine by the interaction of sodium azide and the diazonium sulphate. Nitrogen was evolved immediately, and colourless benzoylethyl-1-aminonaphthyl-4-azoimide was produced.

A more favourable result was obtained from benzoyl-1-aminonaphthalene-4-diazonium chloride and sodium azide in well-cooled aqueous solutions. *Benzoyl-1-aminonaphthalene-4-diazonium azide*, $C_6H_5\cdot CO\cdot NH\cdot C_{10}H_6\cdot N_2\cdot N_3$, was produced as a yellow, crystalline precipitate, practically insoluble in ice-cold water. When treated immediately with alkaline β-naphthol, the weight of benzoyl-1-aminonaphthalene-4-azo-β-naphthol obtained corresponded with 75 per cent. of the amount calculated for the pure diazonium azide.

At 0°, and even more rapidly at higher temperatures, this yellow diazonium azide loses diazo-nitrogen, and becomes converted into the colourless azoimide.

Benzoyl-1-aminonaphthyl-4-azoimide, $C_6H_5\cdot CO\cdot NH\cdot C_{10}H_6\cdot N_3$, crystallises from alcohol in felted masses of colourless needles, melting and decomposing at 167—170°:

0·0944 gave 16·3 c.c. N_2 at 20° and 750 mm. N = 19·49.

$C_{17}H_{12}ON_4$ requires N = 19·45 per cent.

This substance is remarkably sensitive to light, becoming bright yellow after a short exposure.

The authors desire to express their thanks to the Research Grant Committees of the Royal Society and Chemical Society for grants which have partly defrayed the expenses of this investigation.

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CLXXX.—*Dicamphorylphosphinic Acid.*

By Gilbert T. Morgan and Walter R. Moore, A.R.C.S.

The experiments described in the present communication form part of a comparative study of the organic derivatives of the phosphorus family of elements containing camphor nuclei. The condensations of sodium camphor with the trichlorides of arsenic and antimony have already been described (Trans., 1908, **93**, 2144; 1909, **95**, 1473; and this vol., p. 34); this paper deals with the interaction between phosphorus trichloride and sodium camphor.

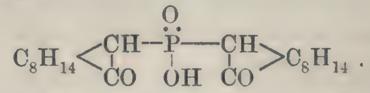
As in the earlier experiments, the condensation was effected in dry toluene, and in this case subsequent treatment with aqueous alkalis removed only one acidic substance, namely, *dicamphorylphosphinic acid*, which was shown to be monobasic by titration with standard alkali hydroxides and by the formation of a series of metallic salts.

The constitution of dicamphorylphosphinic acid was determined by alkaline hydrolysis, when it yielded camphor and sodium orthophosphate, in accordance with the following equation:

$$(C_{10}H_{15}O)_2PO\cdot ONa + 2NaOH = 2C_{10}H_{16}O + Na_3PO_4.$$

This experiment showed that dicamphorylphosphinic acid behaves like dicamphorylarsinic acid, excepting that the phosphorus compound is much more stable than its arsenic analogue towards concentrated alkali hydroxides, for it was only when the water present was removed by evaporation, and the residual alkali had fused, that the hydrolytic decomposition took place. The acid is acted on by phosphorus pentachloride with the evolution of hydrogen chloride and the formation of an acyl chloride, which is still under examination.

These experimental results demonstrate that dicamphorylphosphinic acid has the following constitutional formula:



$$C_8H_{14}\left\langle\begin{array}{ccccc} CH & - & \overset{\overset{O}{\vdots}}{P} & - & CH \\ | & & | & & | \\ CO & & OH & & CO \end{array}\right\rangle C_8H_{14}\,.$$

The group relationship existing between phosphorus, arsenic, and antimony is manifested very clearly by the comparative study of their camphor derivatives. As the atomic weights of these elements increase, the tendency to form the tricamphoryl derivative increases, and the stability of the acid product diminishes. This periodic variation is summarised in the tabulation on p. 1699.

The physical and chemical properties of the metallic dicamphorylphosphinates resemble in general those of the corresponding orthophosphates. The sodium, potassium, and ammonium dicamphorylphosphinates are very soluble in water; those of the heavy metals and metals of the alkaline earths are practically insoluble; *silver dicamphorylphosphinate* is crystalline; the others are obtained as amorphous precipitates. *Lithium dicamphorylphosphinate* is also crystalline, and, like lithium phosphate, is only moderately soluble in water and alkaline solutions.

Condensation Products from Sodium Camphor and the Trichlorides of the Phosphorus Group.

Products.	Phosphorus trichloride.	Arsenic trichloride.	Antimony trichloride.
Dicamphoryl derivatives.	$(C_{10}H_{15}O)_2PO{\cdot}OH$, dicamphorylphosphinic acid, stable in concentrated aqueous alkali hydroxides; decomposed by fused alkali hydroxides.	$(C_{10}H_{15}O)_2AsO{\cdot}OH$, dicamphorylarsinic acid, stable in hot dilute aqueous alkali hydroxides; decomposed by very strong solutions of these alkalis.	—
Tricamphoryl derivatives.	—	$(C_{10}H_{15}O)_3As(OH)_2$, tricamphorylarsinic acid is as stable towards alkalis as the above dicamphoryl derivative.	$(C_{10}H_{15}O)_3SbCl_2$, tricamphorylstibinic chloride, slowly resolved by water into $(C_{10}H_{15}O)_3Sb(OH)_2$, tricamphorylstibinic acid, very unstable, decomposed by dilute aqueous sodium hydroxide and even by boiling water.

Dicamphorylphosphinic Acid, $(C_{10}H_{15}O)_2PO{\cdot}OH$.

Sodium camphor was prepared by the method indicated by Forster (Trans., 1901, **79**, 987), using 75 grams of camphor and 7·5 grams of sodium. This metallic derivative was suspended in dry toluene (200 c.c.), and slowly treated with 29 grams of phosphorus trichloride diluted with two volumes of toluene. The mixture, which was thoroughly shaken, warmed up considerably, and acquired a jelly-like consistence, afterwards regaining its mobility. After one hour, the mixture was gently heated for thirty minutes, and left overnight at the ordinary temperature; 30 c.c. of water were then added to the cooled product of reaction, and the aqueous layer was separated. The toluene layer was now extracted with 2*N*-sodium hydroxide, and the cooled alkaline extract acidified with 2*N*-hydrochloric acid. The crude dicamphorylphosphinic acid thus precipitated has a tendency to become viscid. A further portion of the crude product was obtained by evaporating to dryness the first aqueous extract and the filtrate from the precipitated acid, the residue being extracted with alcohol.

Dicamphorylphosphinic acid does not crystallise so well as dicamphorylarsinic acid, and this difference recalls the behaviour of their inorganic analogues, the hydrated orthophosphoric and orthoarsenic acids, the latter being the more readily crystallisable.

Dicamphorylphosphinic acid is only sparingly soluble in water, ether, or light petroleum (b. p. 40—100°); it dissolves readily in warm benzene, toluene, chloroform, or ethyl alcohol, but only from the last of these solvents does it crystallise at all readily on cooling. The addition of light petroleum to the other solutions facilitates the separation of the acid in a crystalline condition. It separates from absolute alcohol in colourless, nodular crystals, having a prismatic habit, and decomposes at 283°. When titrated with *N*/20-sodium hydroxide, using phenolphthalein as indicator, the acid gave a molecular weight approximating to 366, the value calculated for a monobasic acid:

0·0950 gave 0·2289 CO_2 and 0·0731 H_2O. $C=65·67$; $H=8·61$.
0·2059 „ 0·4948 CO_2 „ 0·1584 H_2O. $C=65·52$; $H=8·61$.
0·1616 „ 0·7552 (P_2O_5,24MoO_3). $P=8·05$.
0·2146 „ 1·0392 (P_2O_5,24MoO_3). $P=8·34$.
$C_{20}H_{31}O_4P$ requires $C=65·67$; $H=8·56$; $P=8·46$ per cent.

A specimen of the acid obtained by repeated crystallisation from absolute alcohol when dissolved in chloroform gave the following reading in the polarimeter:

0·5963, in 25 c.c. of solvent, gave, in a 2-dcm. tube, α_D 7·20°, whence $[\alpha]_D^{20}$ 151·1°.

It was noticed that specimens of the acid crystallised from chloroform gave lower values for $[\alpha]_D$ of about 138·5°; repeated crystallisation from alcohol gradually raised the rotatory power to 149·7° and 151°.

Hydrolytic Decomposition of Sodium Dicamphorylphosphinate.—One gram of this salt was heated in a hard glass flask with excess of concentrated aqueous sodium hydroxide. No appreciable change occurred until the water present had distilled away, when, on further heating, a white sublimate appeared, which was collected in a reflux condenser, and identified as camphor (m. p. 176°); about 50 per cent. of the calculated amount was recovered, the remainder being accidentally lost. The alkaline residue was dissolved in water, and shown to contain sodium orthophosphate by the formation of yellow silver phosphate and crystalline magnesium ammonium phosphate. A small quantity of unaltered dicamphorylphosphinic acid was also recovered.

Salts of Dicamphorylphosphinic Acid.

Sodium dicamphorylphosphinate, $(C_{10}H_{15}O)_2PO·ONa,xH_2O$, was prepared by neutralising the acid exactly with pure aqueous sodium hydroxide and allowing the filtered solution to evaporate in a vacuum desiccator. The residue was a crystalline mass, very soluble in water or alcohol. A portion of the desiccated salt was ignited with concentrated nitric acid to destroy the organic matter present, and a residue of sodium metaphosphate was finally obtained:

0·5962 gave 0·1558 $NaPO_3$. Na = 5·89.
0·5118 „ 0·1352 $NaPO_3$. Na = 5·96.
$C_{20}H_{30}O_4PNa$ requires Na = 5·93 per cent.

Ammonium dicamphorylphosphinate, $(C_{10}H_{15}O)_2PO{\cdot}ONH_4,xH_2O$, produced by adding to the free acid a slight excess of aqueous ammonia and evaporating the solution over concentrated sulphuric acid, is a crystalline substance resembling the sodium salt, and very soluble in water or alcohol. The percentage amount of ammonium present corresponded with the above formula.

The following salts were obtained by double decomposition from sodium dicamphorylphosphinate.

Lithium dicamphorylphosphinate, $(C_{10}H_{15}O)_2PO{\cdot}OLi,2H_2O$, separated in felted masses of small, colourless needles on boiling an aqueous solution of the sodium salt with slight excess of lithium chloride. The filtrate on concentration gave further quantities of this moderately soluble lithium salt, which dissolves more sparingly in warm than in cold water:

0·0734 gave 0·0164 $LiPO_3$. Li = 1·82.
0·5479 „ 0·1123 $LiPO_3$. Li = 1·68.
0·5514 „ 0·0510 H_2O at 140°. H_2O = 9·25.
$C_{20}H_{30}O_4PLi,2H_2O$ requires Li = 1·71; H_2O = 8·82 per cent.

The lithium was estimated by igniting the salt with nitric acid and weighing the residual metaphosphate.

Silver dicamphorylphosphinate, $(C_{10}H_{15}O)_2PO{\cdot}OAg$, when prepared in the dark, separates in minute, white, acicular crystals, which darken on exposure to light, or on warming in their mother liquor. Weighed portions of this salt were digested with concentrated nitric acid, the solution then diluted, and titrated in the usual way with standard ammonium thiocyanate (1 c.c. = 0·01109 Ag):

0·4984 required 10·3 c.c. $NH_4{\cdot}CNS$ solution. Ag = 22·93.
0·4190 „ 8·7 c.c. „ „ Ag = 23·03.
$C_{20}H_{30}O_4PAg$ requires Ag = 22·81 per cent.

Cadmium dicamphorylphosphinate, $[(C_{10}H_{15}O)_2PO{\cdot}O]_2Cd$, prepared by double decomposition, using cadmium chloride, is a white, amorphous precipitate practically insoluble in water. Weighed portions of this salt were digested with nitric acid, the cadmium precipitated as sulphide, redissolved as nitrate or sulphate, and finally precipitated as basic carbonate:

0·5175 gave 0·0806 CdO. Cd = 13·63.
0·7079 „ 0·1060 CdO. Cd = 13·10.

$C_{40}H_{60}O_8P_2Cd$ requires Cd = 13·38 per cent.

Copper dicamphorylphosphinate, $[(C_{10}H_{15}O)_2PO{\cdot}O]_2Cu$, is a blue, amorphous precipitate, insoluble in water, dissolving readily in aqueous ammonia to a deep blue solution:

0·9314 gave 0·0908 CuO. Cu = 7·79.
0·7121 „ 0·0708 CuO. Cu = 7·94.

$C_{40}H_{60}O_8P_2Cu$ requires Cu = 8·01 per cent.

The copper was estimated in a similar manner to the cadmium in the preceding compound.

Lead dicamphorylphosphinate, $[(C_{10}H_{15}O)_2PO{\cdot}O]_2Pb$, is a white, amorphous precipitate obtained by the interaction of sodium dicamphorylphosphinate and lead acetate:

0·6712 gave 0·2118 $PbSO_4$. Pb = 21·57.
0·5326 „ 0·1242 PbO. Pb = 21·60.

$C_{40}H_{60}O_8P_2Pb$ requires Pb = 22·09 per cent.

The dicamphorylphosphinates of magnesium, calcium, strontium, and barium are white, amorphous precipitates, as are also the corresponding salts of zinc, manganese, and aluminium. Mercurous, mercuric, and ferrous dicamphorylphosphinates are white, insoluble substances, the last of these becoming light yellow on exposure to the atmosphere. Ferric dicamphorylphosphinate is a light brown, gelatinous precipitate; the chromium, nickel, and cobalt salts are also insoluble, their colours resembling those of the corresponding phosphates.

The authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this investigation.

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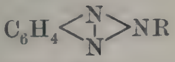
CLXXXI.—*The Constitution of the ortho-Diazoimines. Part I. The Naphthylenediazoimines and their Benzenesulphonyl Derivatives.*

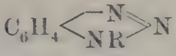
By GILBERT T. MORGAN and WILLIAM GODDEN, B.Sc., A.R.C.S.

THE action of nitrous acid on an aromatic ortho-diamine or on one of its alkyl, aryl, or acyl derivatives leads to the formation of a cyclic diazo-compound, which is represented by one of the following general formulæ, where R is either a hydrogen atom or an alkyl, aryl, or acyl group:



$$C_6H_4{<}\begin{matrix}N\\|\\N\end{matrix}{>}NR$$

(I.)

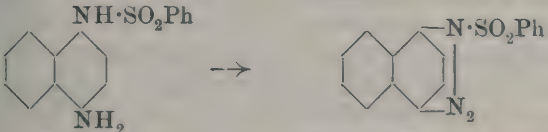


$$C_6H_4{<}\begin{matrix}-N\\NR\end{matrix}{>}N$$

(II.)

In formula I, which is due to Griess (*Ber.*, 1882, **15**, 2195), the substituent R is assumed to have migrated to the nitrogen atom derived from the nitrous acid; according to formula II, proposed by Kekulé (*Lehrbuch*, II, 739), this substituent remains in the position it occupied before the triazole ring was formed.

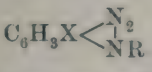
If the latter view of their constitution be accepted, the ortho-diazoimines must be regarded as analogues of the diazoamines, $XN{:}N{\cdot}NHY$, from which, however, they are distinguished invariably by their greater stability, and very frequently by their lack of colour. Moreover, certain acyl derivatives of the para-diamines, benzenesulphonyl-1:4-naphthylenediamine (III), for example, give rise to diazo-compounds (IV), produced by internal condensation, which differ very considerably from the corresponding ortho-diazoimides in being invariably coloured and also hydrolysable by acids (Trans., 1905, **87**, 924):



(III.) (IV.)

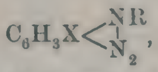
In view of these striking differences existing between the ortho- and para-diazoimides, it seemed of interest to ascertain which of the foregoing formulæ (I and II) is the more appropriate representation of the constitution of the ortho-diazoimines and their *N*-substituted derivatives.

Whichever view be adopted, it is evident that any base having the general formula $(1)NH_2{\cdot}C_6H_4{\cdot}NHR(2)$ can only give rise to one cyclic derivative, $C_6H_4{:}[N_3R]$, but if the molecule be rendered less symmetrical by substitution in the aromatic nucleus as in $(1)NH_2{\cdot}C_6H_3X{\cdot}NHR(2)$, then Kekulé's hypothesis demands two isomerides:



$$C_6H_3X{<}\begin{matrix}N_2\\|\\NR\end{matrix}$$

and



$$C_6H_3X{<}\begin{matrix}NR\\|\\N_2\end{matrix},$$

whereas only one product will result if Griess's view be correct.

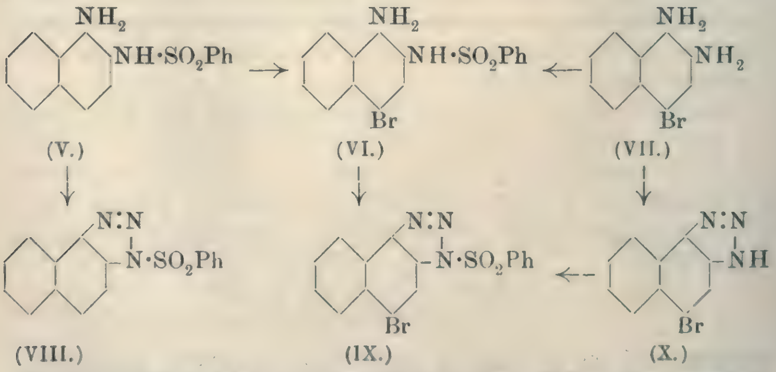
This degree of asymmetry is conveniently produced by working with ortho-naphthylene instead of ortho-phenylene derivatives. According to Kekulé's hypothesis, 1:2-naphthylenediamine and its *N*-substituted derivatives (V) should yield pairs of isomeric diazoimines, whereas 2 : 3-naphthylenediamine and 1 : 8-naphthylenediamine, which also furnish similar diazoimines, should each give only one product. If, however, Griess's formula be correct, only one product should be obtainable from each of these three diamines. The authors' results confirm the formulation advocated by Kekulé.

I.—*The Constitution of the ortho-Diazoimides.*

1. Two isomeric benzenesulphonyl-4-bromo-1 : 2-naphthylenediamines have been prepared, differing only in the position of the benzenesulphonyl group, and these bases, on treatment with nitrous acid, furnish isomeric diazoimides. This result agrees with Kekulé's view, but is inexplicable on Griess's hypothesis.

The more stable of these isomeric diazoimides is obtained by the following series of operations.

Benzenesulphonyl-β-naphthylamine is nitrated to *benzenesulphonyl-1-nitro-β-naphthylamine*, which, on reduction, gives rise to 2-*benzenesulphonyl*-1 : 2-*naphthylenediamine* (V). 2-*Benzenesulphonyl*-4-*bromo*-1 : 2-*naphthylenediamine* (VI) is obtained either by brominating the preceding base or by benzene-sulphonating 4-*bromo*-1 : 2-*naphthylenediamine* (VII), this diamine being prepared from 4-bromo-2-nitro-α-naphthylamine (XV). These alternative methods of preparation determine the constitution of 2-benzenesulphonyl-4-bromo-1 : 2-naphthylenediamine (VI), and treatment of this base with nitrous acid leads to 2-*benzenesulphonyl*-4-*bromonaphthylene*-1-*diazo*-2-*imide* (IX), melting at 209°, a product which also results from 4-bromo-1 : 2-naphthylenediamine (VII) by successive treatment with nitrous acid and benzenesulphonyl chloride:

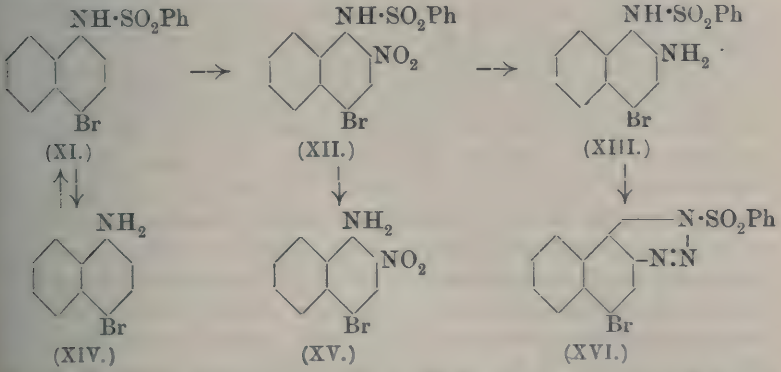


(V.) (VI.) (VII.)

(VIII.) (IX.) (X.)

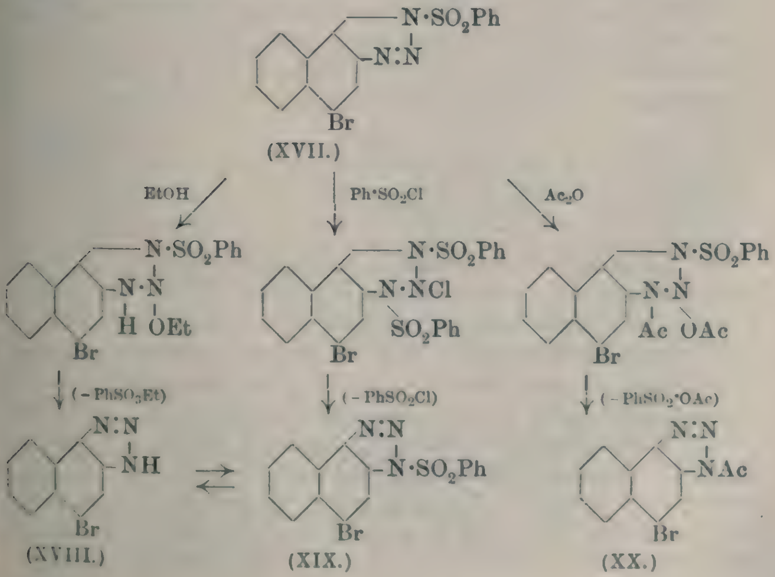
Benzenesulphonyl-4-bromo-α-naphthylamine (XI), the starting point in the synthesis of the less stable isomeric diazoimide, may be prepared from either benzenesulphonyl-α-naphthylamine or 4-bromo-α-naphthylamine (XIV). Nitration leads to *benzenesulphonyl-*

4-*bromo-2-nitro-α-naphthylamine* (XII), the position of the nitro-group being ascertained by hydrolysing the product to 4-bromo-2-nitro-α-naphthylamine (XV):



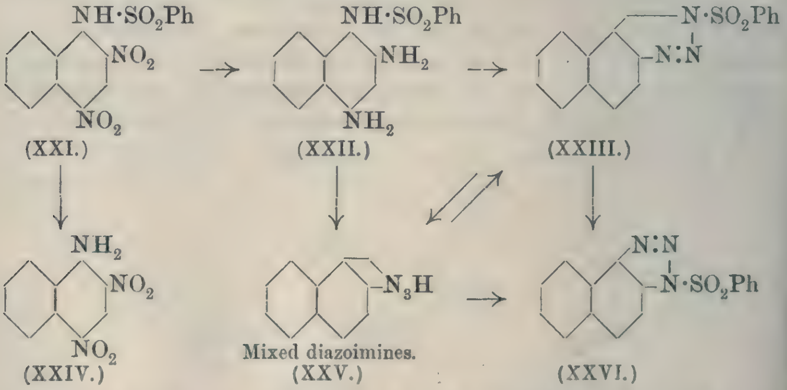
Reduction of the nitro-compound (XII) gives 1-*benzenesulphonyl*-4-*bromo*-1 : 2-*naphthylenediamine* (XIII), and nitrous acid converts this base into 1-*benzenesulphonyl*-4-*bromonaphthylene*-2-*diazo*-1-*imide* (XVI), melting at 159—160°.

The two isomeric diazoimides (IX and XVI) differ not only in melting point, but also in chemical properties. The more fusible isomeride, which contains its acyl group attached to the α-nitrogen atom, is less stable, and the changes undergone by this compound may be indicated by the following diagram:



These three changes have been realised experimentally with considerable facility, and in each case the double linking has shifted from the β- to the α-position. This molecular rearrangement is best explained by assuming that unstable additive products represent the first phase of these reactions, the second step involving respectively the loss of ethyl benzenesulphonate, benzenesulphonyl chloride, and a mixed acyl anhydride. The formation of 4-*bromonaphthylene*-1-*diazo*-2-*imine* (XVIII) takes place at the ordinary temperature when the less stable isomeric diazoimide (XVII) is left in contact with a trace of alcohol. On the contrary, the more stable isomeride (XIX) is hydrolysed to the diazoimine (XVIII) only after prolonged boiling with alcoholic soda. Benzenesulphonation of the diazoimine (XVIII) regenerates the stable diazoimide (XIX), whereas acetylation yields 4-*bromo*-2-*acetylnaphthylene*-1-*diazo*-2-*imide* (XX), which also results from the molecular change of the diazoimide (XVII) in presence of acetic anhydride.

2. The production of a less substituted pair of isomeric acylated ortho-diazoimides was a matter of considerable difficulty, which was finally solved in the following manner:



The nitration of benzenesulphonyl-α-naphthylamine leads to *benzenesulphonyl*-2 : 4-*dinitro*-α-*naphthylamine* (XXI), the position of the nitro-groups being determined by successive hydrolysis to 2 : 4-dinitro-α-naphthylamine (XXIV) and 2 : 4-dinitro-α-naphthol. Reduction of the dinitro-compound gives the very oxidisable 1-*benzenesulphonyl*-1 : 2 : 4-*triaminonaphthalene* (XXII), and diazotisation of this base under carefully regulated conditions yields the required 1-*benzenesulphonylnaphthylene*-2-*diazo*-1-*imide* (XXIII), melting at 159—161°. The acyl group in this product is easily displaced, giving rise either to a mixture of the isomeric 1 : 2-naphthylenediazoimines (XXV) or to the more stable isomeride, *2-benzenesulphonylnaphthylene*-1-*diazo*-2-*imide* (XXVI). This compound, which melts and decomposes at 179°, is more easily obtained by the action of nitrous acid on 2-*benzenesulphonyl*-1 : 2-*naphthylenediamine* (V).

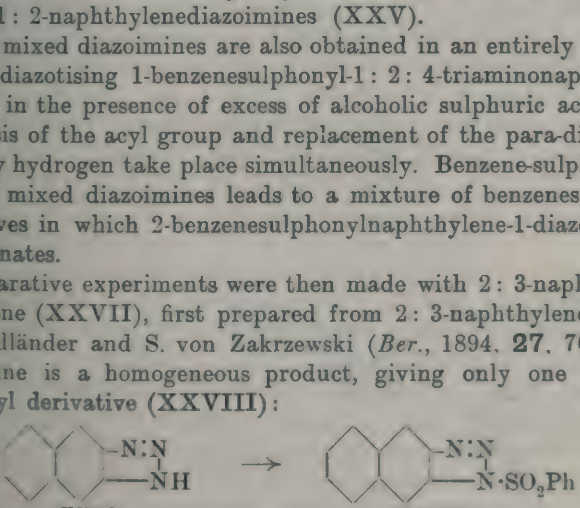
In this pair of isomerides the shifting of the double linking from the β- to the α-position is effected less completely than in the case of the corresponding bromo-derivatives (XVII and XIX), where the bromine atom undoubtedly exerts some directive influence.

II.—*The Constitution of the ortho-Diazoimines.*

The above-mentioned directive influence of the bromine atom is also noticeable in the case of 1 : 2-naphthylenediamine and its 4-bromo-derivative (VII); the latter base gives with nitrous acid a homogeneous product, 4-*bromonaphthylene*-1-*diazo*-2-*imine* (X); the former diamine yields a mixture of isomeric diazoimines, one of which is certainly naphthylene-1-diazo-2-imine, for on benzenesulphonation, the mixed diazoimines furnish a product from which 2-benzenesulphonylnaphthylene-1-diazo-2-imide (VIII and XXVI) has been isolated. The isomeric 1-benzenesulphonylnaphthylene-2-diazo-1-imide (XXIII) has not been identified with certainty in this mixture of benzenesulphonyl derivatives obtained from the mixed 1 : 2-naphthylenediazoimines (XXV).

These mixed diazoimines are also obtained in an entirely different way by diazotising 1-benzenesulphonyl-1 : 2 : 4-triaminonaphthalene (XXII) in the presence of excess of alcoholic sulphuric acid, when hydrolysis of the acyl group and replacement of the para-diazonium group by hydrogen take place simultaneously. Benzene-sulphonation of these mixed diazoimines leads to a mixture of benzenesulphonyl derivatives in which 2-benzenesulphonylnaphthylene-1-diazo-2-imide predominates.

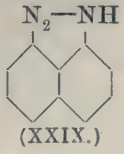
Comparative experiments were then made with 2 : 3-naphthylenediazoimine (XXVII), first prepared from 2 : 3-naphthylenediamine by Friedländer and S. von Zakrzewski (*Ber.*, 1894, **27**, 764); this diazoimine is a homogeneous product, giving only one benzenesulphonyl derivative (XXVIII):



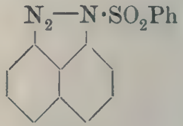
(XXVII.) (XXVIII.)

1 : 8-Naphthylenediamine has already been shown to form only one diazoimine (XXIX) (De Aguiar, *Ber.*, 1874, **7**, 316), and its benzenesulphonyl derivative furnishes a homogeneous product, benzenesulphonyl-1 : 8-naphthylenediazoimide (XXX), which in colour and reactivity resembles closely benzenesulphonyl-1 : 4-naph-

thylenediazoimide (IV) (Morgan and Micklethwait, Trans., 1906, **89**, 4):



(XXIX.)



(XXX.)

Summary.

I. The formula (II) proposed by Kekulé for the ortho-diazoimines is supported by the following observations, most of which were made during the present investigation of the diazo-compounds of the 1: 2-, 2: 3-, and 1: 8-naphthylenediamines and their acyl derivatives.

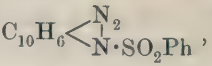
(1) 1: 2-Naphthylenediamine gives rise to a mixture of diazoimines, and two benzenesulphonyl derivatives (XXIII and XXVI) of these 1: 2-naphthylenediazoimines have been isolated.

(2) Two benzenesulphonyl-4-bromo-1: 2-naphthylenediazoimides have been obtained, differing only in the orientation of the acyl group and double linking of the triazole ring (IX and XVI).

(3) 2: 3-Naphthylenediamine furnishes only one diazoimine, which in turn gives one benzenesulphonyl derivative (XXVIII).

(4) 1: 8-Naphthylenediamine and its benzenesulphonyl derivative each give only one diazo-compound (XXIX and XXX).

II. A complete series of benzenesulphonylnaphthylenediazoimides has now been prepared, the general formula being:



$$C_{10}H_6 < \begin{matrix} N_2 \\ | \\ N\cdot SO_2Ph \end{matrix},$$

where $N_2{:}N = 1:2,\ 2:1,\ 2:3,\ 1:4,$ and $1:8$.

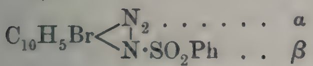
The first three (XXVI, XXIII, and XXVIII) are ortho-diazoimides containing five-membered triazole rings; these isomerides are colourless and not hydrolysable by concentrated acids.

The last two (IV and XXX) are para- and peri-diazoimides, containing respectively seven- and six-membered triazole rings; these isomerides are yellow, and the ring undergoes fission with acids.

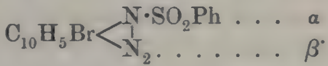
The strain introduced into the molecule by an increase in the number of ring-forming atoms is, in this series of compounds, accompanied by a development of colour.

EXPERIMENTAL.

I.—*The Isomeric Benzenesulphonyl-*4*-bromo-*1 : 2*-naphthylenediazoimides.*



$\mathrm{C_{10}H_5Br}<\begin{matrix}\mathrm{N_2}\ \ldots\ldots\ \alpha\\ \mathrm{N{\cdot}SO_2Ph}\ \ldots\ \beta\end{matrix}$



$\mathrm{C_{10}H_5Br}<\begin{matrix}\mathrm{N{\cdot}SO_2Ph}\ \ldots\ \alpha\\ \mathrm{N_2}\ \ldots\ldots\ \beta\end{matrix}$

2-*Benzenesulphonyl*-4-*bromo*-1 : 2-*naphthylenediamine* (VI), which separated slowly on mixing chloroform solutions of bromine (1 mol.) and 2-benzenesulphonyl-1 : 2-naphthylenediamine (1 mol.), was washed with light petroleum and converted into its hydrochloride, this salt being then dissolved in alcohol and reprecipitated on the addition of water. The base set free with ammonia crystallised from alcohol in colourless, slender needles, melting and decomposing at 171°:

0·1778 gave 11·6 c.c. N_2 at 16° and 748·5 mm. N = 7·49.

0·2326 „ 0·1151 AgBr. Br = 21·05.

$C_{16}H_{13}O_2N_2BrS$ requires N = 7·43; Br = 21·22 per cent.

The yield of the base obtained by the foregoing method was only 30 per cent. of the calculated amount, and the bromination went even less smoothly in glacial acetic acid. The position of the bromine atom in this acylated amine was determined by preparing the base from 4-bromo-1 : 2-naphthylenediamine (VII) in the following way.

4-Bromo-2-nitroaceto-α-naphthalide (m. p. 230°) was prepared both by the nitration of 4-bromoaceto-α-naphthalide and by the bromination of 2-nitroaceto-α-naphthalide (m. p. 199°); these reactions were carried out in warm glacial acetic acid, and the former process was found to be the more convenient.

The bromo-compound (50 grams) suspended in 150 c.c. of glacial acetic acid at 60° was treated with 20 c.c. of nitric acid (D 1·42) diluted with 50 c.c. of glacial acetic acid, and previously freed from nitrous acid by the addition of a small quantity of carbamide. On hydrolysis with alcoholic ammonia, or less preferably with alcoholic potash or sulphuric acid, this bromoacetyl derivative yielded 4-bromo-2-nitro-α-naphthylamine (m. p. 200°), which was also prepared in quantitative yield by heating 1 gram of benzenesulphonyl-4-bromo-2-nitro-α-naphthylamine (XII) with 20 c.c. of alcoholic ammonia for three hours at 180°.

A singular result was obtained on attempting to hydrolyse 4-bromo-2-nitroaceto-α-naphthalide with alcoholic ammonia at 210° in a steel tube with leaden washers. The product, when precipitated with water and crystallised from alcohol, separated in well-defined, silvery-grey needles, melting at 224—226°, and containing only 4·9 per cent. of nitrogen; this substance was also obtained on reducing with zinc dust and ammonia, some impure specimens of 4-bromo-2-nitro-α-naphthylamine.

4-*Bromo*-1 : 2-*naphthylenediamine*, $NH_2 \cdot C_{10}H_5Br \cdot NH_2$, was prepared by reducing pure 4-bromo-2-nitro-α-naphthylamine (XV) with zinc dust and ammonium chloride in hot dilute alcohol, the reducing agent being slowly introduced until the colour of the solution was discharged. The filtered solution was poured on to ice, and the precipitate, when crystallised from benzene, separated in yellowish needles, melting at 104—106°:

0·1487 gave 14·95 c.c. N_2 at 18° and 755 mm. N = 11·53.
0·2124 „ 0·1672 AgBr. Br = 33·49.
$C_{10}H_9N_2Br$ requires N = 11·81; Br = 33·74 per cent.

When dissolved in benzene containing triethylamine and treated with benzenesulphonyl chloride at 90—100°, 4-bromo-1 : 2-naphthylenediamine undergoes acylation in the β-amino-group only, the product (m. p. 167—168°) being identical with 2-benzenesulphonyl-4-bromo-1 : 2-naphthylenediamine (VI, p. 1704). This result confirms the constitutional formula (*loc. cit.*) ascribed to this acylated diamine.

2-*Benzenesulphonyl*-4-*bromonaphthylene*-1-*diazo*-2-*imide* (IX, p. 1704).

When dissolved in cold alcohol and treated successively with concentrated hydrochloric acid (0·5 c.c.) and amyl nitrite (0·15 gram), 2-benzenesulphonyl-4-bromo-1 : 2-naphthylenediamine (0·5 gram) furnishes a violet precipitate which, after crystallisation from ethyl acetate and alcohol, separated in colourless, lustrous needles, melting at 209°:

0·1579 gave 0·2874 CO_2 and 0·0356 H_2O. C = 49·64; H = 2·50.
0·2048 „ 19·2 c.c. N_2 at 16° and 748·5 mm. N = 10·76.
0·2452 „ 0·1176 AgBr. Br = 20·41.
$C_{16}H_{10}O_2N_3BrS$ requires C = 49·48; H = 2·58; N = 10·82; Br = 20·62 per cent.

This diazoimide was produced from both preparations of 2-benzenesulphonyl-4-bromo-1 : 2-naphthylenediamine, namely, that obtained by acylating 4-bromo-1 : 2-naphthylenediamine, and the other resulting from the bromination of 2-benzenesulphonyl-1 : 2-naphthylenediamine. The identical results obtained establish the constitution of the diazoimide.

Benzenesulphonyl-4-*bromo*-α-*naphthylamine*,

$C_{10}H_6Br \cdot NH \cdot SO_2 \cdot C_6H_5$,

was prepared by the following methods.

(1) 4-Bromo-α-naphthylamine, obtained by brominating aceto-α-naphthalide and hydrolysing the bromo-derivative with concentrated aqueous potassium hydroxide, could not be converted into its benzenesulphonyl derivative by either the Schotten-Baumann reaction or Witt and Schmitt's method (p. 1714). This acylation was, however, readily effected by mixing molecular proportions of the base and benzenesulphonyl chloride in warm dehydrated pyridine, the solution being boiled for three hours. The product was extracted successively with cold dilute hydrochloric acid and warm aqueous potassium hydroxide, the benzenesulphonyl derivative being precipitated from the cooled alkaline extract by dilute acetic acid.

When crystallised from alcohol, benzenesulphonyl-4-bromo-α-naphthylamine separated in colourless needles with a violet tinge, the melting point being 148—149°; the yield was about 85 per cent. of the calculated amount:

0·3572 gave 12·7 c.c. N_2 at 23° and 767 mm. N = 4·04.
0·4684 „ 0·2445 AgBr. Br = 22·21.
$C_{16}H_{12}O_2NBrS$ requires N = 3·87; Br = 22·10 per cent.

(2) Benzenesulphonyl-4-bromo-α-naphthylamine was subsequently prepared by the direct bromination of benzenesulphonyl-α-naphthylamine, this compound, like its β-isomeride, being produced by Witt and Schmitt's method (p. 1714). The bromination was effected in warm glacial acetic acid, when pure benzenesulphonyl-4-bromo-α-naphthylamine separated.

Benzenesulphonyl-2-nitro-4-bromo-α-naphthylamine,

$$C_{10}H_5Br(NO_2)\cdot NH\cdot SO_2Ph,$$

was obtained in almost quantitative yield by shaking for two hours a mixture of two parts of the foregoing benzenesulphonyl derivative, one part of nitric acid (D 1·42), and 8—9 parts of glacial acetic acid. When crystallised from alcohol, the product separated in clusters of transparent, prismatic needles, softening at 195° and melting at 198°:

0·3302 gave 19·8 c.c. N_2 at 26° and 769 mm. N = 6·74.
0·4535 „ 0·2075 AgBr. Br = 19·46.
0·2463 „ 0·1333 $BaSO_4$. S = 7·43.
$C_{16}H_{11}O_4N_2BrS$ requires N = 6·88; Br = 19·65; S = 7·86 per cent.

This nitro-compound was suspended in about 30 parts of boiling 2 per cent. acetic acid, and reduced with excess of iron filings. After neutralising the solution with sodium carbonate, the insoluble residue was extracted with alcohol.

1-*Benzenesulphonyl-4-bromo*-1 : 2-*naphthylenediamine*,

$$C_{10}H_5Br(NH_2)\cdot NH\cdot SO_2Ph,$$

was precipitated by water from the alcoholic filtrate in almost colourless plates, and crystallised from acetic acid in colourless needles, melting and decomposing at 220° (yield, 75 per cent.):

0·3128 gave 21·5 c.c. N_2 at 25° and 764 mm. N = 7·71.
0·3910 „ 0·1929 AgBr. Br = 20·99.
$C_{16}H_{13}O_2N_2BrS$ requires N = 7·43; Br = 21·22 per cent.

This base was converted into the diazoimide (XVI) by adding successively to its alcoholic solution hydrochloric acid and amyl nitrite. On shaking, a white precipitate slowly separated, which, after crystallisation from alcohol and finally from benzene, melted at 159—160°:

0·1427 gave 0·2569 CO_2 and 0·0361 H_2O. C = 49·09; H = 2·81.
0·2000 „ 19·1 c.c. N_2 at 20° and 744 mm. N = 10·70.
0·4051 „ 0·1937 AgBr. Br = 20·35.
$C_{16}H_{10}O_2N_3BrS$ requires C = 49·48; H = 2·58; N = 10·82; Br = 20·62 per cent.

It was found impossible to remove bromine from this compound without producing destructive changes leading to ill-defined products.

The Displacement of the Benzenesulphonyl Group in 1-*Benzenesulphonyl*-4-*bromonaphthylene*-2-*diazo*-1-*imide* (compare diagram on p. 1705).

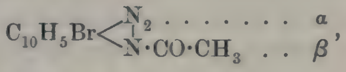
The five-membered triazole ring in the two isomeric benzenesulphonyl-4-bromonaphthylenediazoimides (IX and XVI), like that in the benzenesulphonyl derivatives of 1 : 2- and 2 : 3-naphthylenediazoimines (pp. 1715, 1718), does not undergo fission when the foregoing compounds are mixed with cold concentrated hydrochloric acid, but the acyl groups in these two isomerides are not held equally firmly in their respective triazole rings.

2-Benzenesulphonyl-4-bromonaphthylene-1-diazo-2-imide is not affected by warming with acetic anhydride or alcohol, and when crystallised from alcohol it remains unchanged at the ordinary temperature for an indefinite time. 1-Benzenesulphonyl-4-bromonaphthylene-2-diazo-1-imide, on the contrary, readily loses its acyl group. When containing a trace of alcohol, a specimen of this substance slowly becomes viscid at the ordinary temperature, and the product, after crystallisation from alcohol, separates in colourless leaflets, containing no sulphur, and melting indefinitely at about 296°:

0·0850 gave 12·1 c.c. N_2 at 17° and 772·5 mm. N = 16·81.
0·1370 „ 0·1030 AgBr. Br = 31·99.
$C_{10}H_6N_3Br$ requires N = 16·93; Br = 32·25 per cent.

That this substance is 4-*bromonaphthylene*-1-*diazo*-2-*imine* (X) is proved by preparing it directly from 4-bromo-1 : 2-naphthylenediamine and by benzene-sulphonating it, when the more stable 2-benzenesulphonyl-4-bromonaphthylene-1-diazo-2-imide (IX) is produced. This 2-benzenesulphonyl derivative undergoes hydrolysis with boiling alcoholic soda, and is again converted into 4-bromo-1 : 2-naphthylene-1-diazo-2-imine.

An acetylated diazoimide, 4-*bromo*-2-*acetylnaphthylene*-1-*diazo*-2-*imide*,



$$C_{10}H_5Br{<}\begin{array}{l} N_2 \; \cdots\cdots\cdots \; \alpha \\ | \\ N{\cdot}CO{\cdot}CH_3 \; \cdot\cdot \; \beta \end{array},$$

was obtained by boiling 1-benzenesulphonyl-4-bromonaphthylene-2-diazo-1-imide with acetic anhydride for three minutes; it crystallised from this solution in well-defined, colourless needles, melting at 158°:

0·1505 gave 18·6 c.c. N_2 at 22° and 760 mm. N = 14·00.

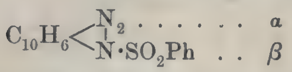
$C_{12}H_8ON_3Br$ requires N = 14·48 per cent.

The position of the acetyl group was ascertained by dissolving 4-bromonaphthalene-1-diazo-2-imine (m. p. 296°) in glacial acetic acid containing acetic anhydride, and boiling the solution for one hour. On cooling, small, colourless needles separated, which melted at 158°, and did not depress the melting point of the preceding preparation.

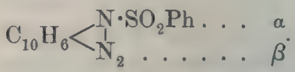
The Direct Conversion of 1-*Benzenesulphonyl*-4-*bromonaphthylene*-2-*diazo*-1-*imide into* 2-*Benzenesulphonyl*-4-*bromonaphthylene*-1-*diazo*-2-*imide.*

The less stable isomeride melting at 156° (XVI) was dissolved in dry benzene, and the solution boiled for two hours with excess of triethylamine and benzenesulphonyl chloride. The solution was left to evaporate at the ordinary temperature, and the residue extracted with alcohol, four fractions being collected The first two fractions melted at 286°, and were identified as 4-bromonaphthylene-1-diazo-2-imine; the last two melted at 209°, and were identified as 2-benzenesulphonyl-4-bromonaphthylene-1-diazo-2-imide. These results show that the 1-benzenesulphonyl derivative is partially transformed by benzenesulphonyl chloride into the isomeric 2-benzenesulphonyl derivative, whilst the substance remaining unchanged is hydrolysed by the alcohol used in the extraction.

II.—*The Isomeric Benzenesulphonyl*-1 : 2-*naphthylenediazoimides.*



$$C_{10}H_6{<}\begin{matrix}N_2 \ldots\ldots\ \alpha \\ | \\ N\cdot SO_2Ph\ \ldots\ \beta\end{matrix}$$



$$C_{10}H_6{<}\begin{matrix}N\cdot SO_2Ph \ldots\ \alpha \\ | \\ N_2 \ldots\ldots\ \beta\end{matrix}$$

Benzenesulphonyl-β-naphthylamine (m. p. 104—105°), the starting point in the preparation of the former of these isomerides (VIII), was obtained by Witt and Schmitt's method (*Ber.*, 1894, **17**, 2371) from β-naphthylamine, benzenesulphonyl chloride, and anhydrous sodium acetate, the product being purified through its sodium salt and crystallisation from alcohol or benzene.

Benzenesulphonyl-1-*nitro*-β-*naphthylamine*,

$$NO_2\cdot C_{10}H_6\cdot NH\cdot SO_2Ph,$$

is produced by shaking together the foregoing sulphonamide and a slight excess of nitric acid (D 1·42) diluted with 5 parts of warm glacial acetic acid, the reaction being completed after one or two hours. The precipitated nitro-compound, when crystallised repeatedly from hot glacial acetic acid, melts at 155·5° (yield about 90 per cent.):

0·2467 gave 17·7 c.c. N_2 at 20° and 772·5 mm. N = 8·36.
0·3289 „ 0·2276 $BaSO_4$. S = 9·46.
0·3534 „ 0·2443 $BaSO_4$. S = 9·48.
$C_{16}H_{12}O_4N_2S$ requires N = 8·53; S = 9·75 per cent.

2-*Benzenesulphonyl*-1 : 2-*naphthylenediamine* (V).

The above nitro-compound was reduced most effectively by adding slowly excess of iron filings to the substance suspended in hot 2 per cent. hydrochloric acid. After neutralising with sodium carbonate, the insoluble residue was extracted with alcohol, and the base precipitated from the filtrate by diluting with water. The product separated from alcohol in white needles, and from glacial acetic acid in stout prisms (yield 50 to 60 per cent.):

0·2759 gave 22·8 c.c. N_2 at 25° and 768 mm. N = 9·32.
0·3900 „ 0·2891 $BaSO_4$. S = 10·27.
$C_{16}H_{14}O_2N_2S$ requires N = 9·39; S = 10·73 per cent.

The purified base melts and decomposes at 215°, and rapidly darkens on exposure to air.

The *formyl* derivative obtained by warming the base with slightly diluted formic acid crystallised from water in colourless leaflets, melting at 176—177°.

*2-Benzenesulphonylnaphthylene-*1*-diazo-*2*-imide* (VIII).

The somewhat unstable character of the preceding base was manifested by the behaviour of its hydrochloride towards amyl nitrite in alcoholic solution, when the diazoimide produced was discoloured by a violet decomposition product. A more satisfactory result was obtained by dissolving the base in glacial acetic acid, and adding successively an equal weight of concentrated hydrochloric acid and rather more than the calculated amount of 20 per cent. aqueous sodium nitrite. The product, which was partly deposited and partly precipitated after dilution with water, crystallised from alcohol or glacial acetic acid, and melted with decomposition at 175—176°:

0·0878 gave 0·1991 CO_2 and 0·0289 H_2O. C=61·84; H=3·65.
0·0886 „ 11·0 c.c. N_2 at 25° and 764 mm. N=13·93.
0·3660 „ 0·2660 $BaSO_4$. S=9·98.
$C_{16}H_{11}O_2N_3S$ requires C=62·13; H=3·56; N=13·59; S=10·35 per cent.

The diazoimide is very soluble in ethyl acetate, but dissolves only sparingly in benzene and other dry solvents.

1*-Benzenesulphonylnaphthylene-*2*-diazo-*1*-imide.*

*Benzenesulphonyl-*2 : 4*-dinitro-α-naphthylamine,*

$C_{10}H_5(NO_2)_2\cdot NH\cdot SO_2Ph$,

was produced by nitrating benzenesulphonyl-α-naphthylamine with a moderate excess (2·5 mols.) of nitric acid (D 1·42) in five parts of glacial acetic acid. Usually the reaction proceeded in the cold even when the acyl derivative was merely suspended in the diluent, but sometimes the mixture required warming. The addition of a few drops of alcohol also served to accelerate the change.

When crystallised from alcohol, the dinitro-compound separated in felted masses of pale yellow needles, melting at 185—186°:

0·1966 gave 19·1 c.c. N_2 at 23° and 755·5 mm. N=10·88.
0·3341 „ 0·2113 $BaSO_4$. S=8·68.
$C_{16}H_{11}O_6N_3S$ requires N=11·26; S=8·57 per cent.

The position of one nitro-group in this compound was determined by preparing the substance from benzenesulphonyl-4-nitro-α-naphthylamine * by treatment with nitric acid (D 1·42) diluted with glacial acetic acid, as in the preceding experiment.

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* This compound, which is readily prepared by adding benzenesulphonyl chloride to a cold pyridine solution of 4-nitro-α-naphthylamine, has now been found to melt at 173°, the melting point (158°) previously given being too low (Trans., 1905, **87**, 928).

The position of the second group was ascertained by hydrolysing the dinitro-compound. This process was carried out in two ways. Prolonged boiling with alcoholic sulphuric acid removed the acyl group, leaving 2:4-dinitro-α-naphthylamine, crystallising in yellow needles, and melting at 235—238° (Meldola, *Ber.*, 1886, **19**, 2683; Hübner, *Annalen*, 1881, **208**, 330). More drastic hydrolysis with alcoholic soda led to the replacement of the whole benzenesulphonylamino-group, $C_6H_3{\cdot}SO_2{\cdot}NH$, by hydroxyl with the formation of 2:4-dinitro-α-naphthol (m. p. 143°). These reactions demonstrate conclusively the constitution of benzenesulphonyl-2:4-dinitro-α-naphthylamine.

1-*Benzenesulphonyl*-1:2:4-*triaminonaphthalene* (XXII).

The reduction of the preceding dinitro-compound presented considerable difficulty, owing to the very oxidisable nature of the resulting triamine.* The best results were obtained by reducing the dinitro-compound in lots of 2 grams dissolved in 50 c.c. of alcohol and 10 c.c. of water containing 2 grams of ammonium chloride. Fresh zinc dust (4—5 grams) was added rapidly, and the mixture boiled until the yellow colour of the solution was discharged, the success of the experiment depending on the rapidity of the reduction. The solution was filtered quickly on to crushed ice in an atmosphere of carbon dioxide, and the crude triamine which separated was purified from a reddish-brown by-product by extraction with toluene. The base separated from toluene or chloroform, on adding light petroleum, in felted, colourless needles, which assumed a light brown colour on exposure to air:

0·1108 gave 13·0 c.c. N_2 at 20° and 763 mm. N = 13·48.
0·1585 „ 0·1224 $BaSO_4$. S = 10·60.
$C_{16}H_{15}O_2N_3S$ requires N = 13·41; S = 10·22 per cent.

1-Benzenesulphonyl-1:2:4-triaminonaphthalene melted at 195—197°, and dissolved readily either in acids or in aqueous alkali hydroxides, being reprecipitated from its alkaline solutions by dilute acetic acid. In aqueous solution the base was very unstable, and ferric chloride oxidised it to a red, insoluble substance.

Conversion of 1-*Benzenesulphonyl*-1:2:4-*triaminonaphthalene into* 1-*Benzenesulphonylnaphthylene*-2-*diazo*-1-*imide*.

After many unsuccessful attempts to diazotise 1-benzenesulphonyl-1:2:4-triaminonaphthalene without removing the acyl group, it was finally discovered that the diazotisation and elimination of the diazo-group could be effected in one stage by operating in the following manner. The triamine (0·4 gram) dissolved in 30 c.c. of alcohol, containing 0·3 c.c. of concentrated hydrochloric acid, was treated with excess of 33 per cent. ethyl nitrite (3 c.c.), the solution being cooled in ice and salt. After fifteen to twenty minutes, the solution, which gave no azo-reaction with alkaline β-naphthol, was diluted with water. The dried precipitate, when extracted with petroleum (b. p. 100—120°), separated from this solvent in light orange needles, melting at 159—161°:

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* The authors desire to express their thanks to Miss F. M. G. Micklethwait for her invaluable assistance in the later stages of this work.

0·1386 gave 0·3150 CO_2 and 0·0498 H_2O. C=61·97; H=3·99.
0·1070 „ 13·2 c.c. N_2 at 24° and 760 mm. N=13·80.
0·2190 „ 0·1646 $BaSO_4$. S=10·32.
$C_{16}H_{11}O_2N_3S$ requires C=62·13; H=3·56; N=13·59; S=10·35 per cent.

1-*Benzenesulphonylnaphthylene*-2-*diazo*-1-*imide* (XXIII) loses its acyl group fairly readily, and the crude product of the preceding experiment always contains a certain amount of 1:2-naphthylenediazoimine, which remains insoluble on extracting with petroleum. This diazoimine depresses the melting point of its isomeride, and differs from it in the ease with which it loses its acyl group. When warmed with alcohol, this hydrolytic change occurred, and the final product, which was then entirely soluble in aqueous sodium hydroxide, melted over a considerable range of temperature (160—190°), and thus resembled the mixed diazoimines obtained from 1:2-naphthylenediamine (p. 1719).

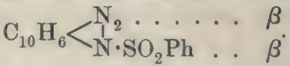
4-*Iodo-α-naphthylamine*, $C_{10}H_6I\cdot NH_2$.

Many unsuccessful attempts were made to prepare benzenesulphonyl-2-nitro-α-naphthylamine. In one of these, 4-nitro-α-naphthylamine was taken as the starting point, and converted through the diazo-reaction into 4-iodo-1-nitronaphthalene (Meldola, Trans., 1885, **47**, 497). This compound was then reduced with zinc dust and glacial acetic acid, the 4-iodo-α-naphthylamine being obtained in the form of its colourless sulphate. The base itself was isolated by shaking this salt with chloroform and aqueous ammonia, when the organic solvent removed the base, which is unstable in a moist condition. The chloroform extract was quickly dried with calcium chloride, and the 4-iodo-α-naphthylamine precipitated by the addition of light petroleum in colourless needles, having a pink tinge; further darkening occurred on exposure to moist air:

0·4032 gave 17·3 c.c. N_2 at 17° and 772·5 mm. N=5·06.
0·2352 „ 0·2042 AgI. I=46·92.
$C_{10}H_8NI$ requires N=5·20; I=47·21 per cent.

4-Iodo-α-naphthylamine melts and decomposes at 82—84°, and slowly becomes resinous even at the ordinary temperature. It was too unstable to undergo acylation with benzenesulphonyl chloride.

Benzenesulphonylnaphthylene-2 : 3-*diazoimide*,



$$C_{10}H_6<\begin{matrix} N_2 \;.\;.\;.\;.\;.\;. & \beta \\ | & \\ N\cdot SO_2Ph \;.\;. & \beta \end{matrix}.$$

2 : 3-Naphthylenediamine (m. p. 195°) was prepared by heating 2 : 3-dihydroxynaphthalene with 10 parts of concentrated ammonia for twelve hours at 240°. In successful experiments the yield was very good, but comparatively few glass tubes could be obtained sufficiently strong to withstand the very high pressures attained at this temperature. At lower temperatures the product was mixed with 3-amino-β-naphthol, whilst in steel tubes at higher temperatures the metal seemed to exert some reducing action on the diamine, which was thus rendered very impure.

Naphthylene-2 : 3-diazoimine, produced by adding the calculated amount of aqueous sodium nitrite to a solution of the diamine in very dilute hydrochloric acid, separated as a yellow precipitate, which was purified through its sodium salt and by crystallisation from light petroleum (compare Friedländer and Zakrzewski, *Ber.*, 1894, **27**, 764).

This diazoimine can be benzene-sulphonated by the Schotten-Baumann reaction. The product separated as a crystalline precipitate, and was extracted with petroleum.

Benzenesulphonylnaphthylene-2 : 3-*diazoimide* crystallised in colourless needles, which gradually assumed an orange tinge; it melted at 156—158°:

0·1050 gave 12·5 c.c. N_2 at 17° and 758 mm. N = 13·78.

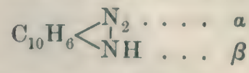
0·1492 „ 0·1146 $BaSO_4$. S = 10·56.

$C_{16}H_{11}O_2N_3S$ requires N = 13·59; S = 10·35 per cent.

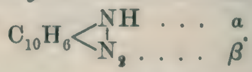
The alkaline filtrate from the benzenesulphonylnaphthylene-2 : 3-diazoimide was acidified with dilute acetic acid, when some unchanged naphthylene-2 : 3-diazoimine was recovered, which melted sharply at 187°.

These experiments indicate that 2 : 3-naphthylenediamine yields a homogeneous diazoimine, which in turn gives only one benzenesulphonyl derivative.

III. *The Isomeric* 1 : 2-*Naphthylenediazoimines*,



$$C_{10}H_6<\begin{matrix} N_2 \;.\;.\;.\;. & \alpha \\ | & \\ NH \;.\;.\;. & \beta \end{matrix}$$



$$C_{10}H_6<\begin{matrix} NH \;.\;.\;. & \alpha \\ | & \\ N_2 \;.\;.\;.\;. & \beta \end{matrix}.$$

On treatment with nitrous acid or ethyl or amyl nitrite in acid solutions, 1 : 2-naphthylenediamine behaves quite differently from its isomeride, 2 : 3-naphthylenediamine; for whereas the latter gives rise to one homogeneous substance, 2 : 3-naphthylenediazoimine, the former diamine yields a mixed product melting over a considerable range of temperature. The earlier experiments were made with the sparingly soluble 1 : 2-naphthylenediamine sulphate, this salt being suspended in cold glacial acetic acid and treated with excess of 20 per cent. sodium nitrite. The salt dissolved to a brownish-yellow solution, and the best preparations of diazoimine were obtained by pouring this liquid into ice-cold water and partly neutralising the acid with dilute ammonia. The crude pale brownish-yellow product sintered at 158°, and melted at 174°:

0·1018 gave 21·0 c.c. N_2 at 17° and 772 mm. N = 24·34.

$C_{10}H_7N_3$ requires N = 24·85 per cent.

Another preparation was obtained by mixing the sulphate intimately with 20 per cent. aqueous sodium nitrite and adding the mixture to glacial acetic acid. The granular, pale brown precipitate which separated softened at 260° and melted at 285°:

0·1636 gave 35·2 c.c. N_2 at 18° and 746 mm. N = 24·38.

This analysis indicates that the two preparations, although differing considerably in melting point, are nevertheless isomeric; they both dissolve in aqueous sodium hydroxide, and are reprecipitated by acids in an almost colourless condition. As these products appeared to be mixtures, an attempt was made to separate their constituents by extraction with anhydrous benzene, and a soluble portion, sintering at 150—160°, and melting indefinitely at 170—180°, was separated from an insoluble part sintering at 260—270° and melting at 280—285°. Nitrogen determinations in these fractions showed, however, that partial decomposition and loss of nitrogen had occurred.

1 : 2-Naphthylenediamine was now prepared by reducing with stannous chloride the azo-compound, 1-sulphobenzeneazo-β-naphthylamine, $SO_3H\cdot C_6H_4\cdot N_2\cdot C_{10}H_7\cdot NH_2(\beta)$. The diamine was suspended in alcohol, and treated successively with concentrated hydrochloric acid and ethyl nitrite; an evanescent green coloration developed, the solid passed into solution, and the soluble product was precipitated fractionally by the addition of iced water and sodium chloride. The first fraction sintered at 150—180°, and melted indefinitely at 210—225°; the second main fraction sintered at 100°, melted at 120°, and was readily soluble in benzene. These fractions were treated with benzenesulphonyl chloride and triethylamine in dry benzene. The first fraction yielded an ill-defined product, the second gave a benzenesulphonyl derivative melting at 175—177°, which was identical with 2-benzenesulphonylnaphthylene-2-diazo-1-imide, as indicated by mixed melting points.

The diazotisation of 1 : 2-naphthylenediamine with sodium nitrite in dilute hydrochloric acid gave a diazoimine melting at 110—120°. This product, when benzene-sulphonated, also yielded 2-benzenesulphonylnaphthylene-2-diazo-1-imide.

The Conversion of 1-*Benzenesulphonyl*-1 : 2 : 4-*triaminonaphthalene into the Mixed* 1 : 2-*Naphthylenediazoimines.*

One gram of the triamine dissolved in 10 c.c. of concentrated sulphuric acid, diluted with 5 grams of ice, was treated with 0·6 gram of solid sodium nitrite at $-5°$ to 0°. Five grams of ice were then added, and the diazonium sulphate precipitated with cooled alcohol and ether. The pale yellow salt was washed with ether and divided into two parts; one was boiled with alcohol alone, and the other with alcohol containing finely divided copper powder. In the latter case the diazonium salt was rapidly decomposed, and on cooling and diluting the solution deposited a diazoimine soluble in aqueous sodium hydroxide, and melting at 185°. The diazonium salt, when boiled with alcohol alone, resisted decomposition for a much longer time, and on cooling and diluting, a diazoimine soluble in aqueous sodium hydroxide was obtained, but in this case melting at 265°:

0·1110 gave 23·9 c.c. N_2 at 749 mm. and 19°. $N = 24·38$.

$C_{10}H_7N_3$ requires $N_2 = 24·85$ per cent.

This experiment was repeated several times, and similar products were obtained, with melting points ranging from 180° to 270°.

The Benzenesulphonyl Derivatives from the Mixed 1 : 2-*Naphthylenediazoimines.*

The mixed 1 : 2-naphthylenediazoimines (m. p. 180° and 270°), prepared from 1-benzenesulphonyl-1 : 2 : 4-triaminonaphthalene, when warmed with benzenesulphonyl chloride in dry toluene containing excess of triethylamine, yielded a benzenesulphonyl derivative, melting at 175—177°, which was identical with 2-benzenesulphonyl-1-diazo-2-imide obtained directly from 2-benzenesulphonyl-1 : 2-naphthylenediamine.

The mixed 1 : 2-naphthylenediazoimines obtained from 1 : 2-naphthylenediamine were converted into the benzenesulphonyl derivatives by treatment with benzenesulphonyl chloride and triethylamine in boiling toluene. The product was separated into two fractions, one separating from the toluene together with the triethylamine hydrochloride, the other remaining in solution.

The less soluble fraction was crystallised from light petroleum

(b. p. 80—100°), and was then found to be identical with 2-benzenesulphonyl-1-diazo-2-imide (m. p. 177°):

0·1402 gave 0·1066 $BaSO_4$. S = 10·44.
0·1000 „ 12·1 c.c. N_2 at 19·5° and 750 mm. N = 13·70.
$C_{16}H_{11}O_2N_3S$ requires S = 10·35; N = 13·59 per cent.

The more soluble fraction, after recrystallisation from light petroleum (b. p. 80—100°), separated in a mass of small, almost colourless crystals, melting somewhat indefinitely at 157—160°:

0·1662 gave 0·1290 $BaSO_4$. S = 10·63.
0·1072 „ 12·8 c.c. N_2 at 17° and 742 mm. N = 13·53.
$C_{16}H_{11}O_2N_3S$ requires S = 10·35; N = 13·59 per cent.

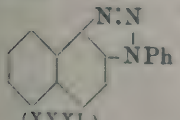
These analyses indicate that the more fusible product, obtained by benzene-sulphonating the mixed 1 : 2-naphthylenediazoimines, is isomeric with the less fusible product, 2-benzenesulphonyl-1-diazo-2-imide.

Comparison of this more fusible product with 1-benzenesulphonylnaphthylene-2-diazo-1-imide (p. 1715) showed that the former depresses the melting point of the latter, and is probably a mixture of the two isomeric benzenesulphonyl-1 : 2-naphthylenediazoimides.

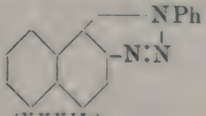
This view is confirmed by experiments made on the action of benzenesulphonyl chloride on 1-benzenesulphonylnaphthylene-2-diazo-1-imide in the presence of triethylamine. When these reagents are heated together in dry toluene, the product is evidently a mixed benzenesulphonyl derivative corresponding with the more fusible fraction obtained from the mixed 1 : 2-naphthylenediazoimines. It is evidently impossible to separate the two benzenesulphonyl derivatives by fractional crystallisation from petroleum, benzene, or other solvents, as the crystals obtained invariably consist either of the less fusible 2-benzenesulphonylnaphthylene-1-diazo-2-imide (m. p. 177°) or of mixtures of this isomeride with 1-benzenesulphonylnaphthylene-2-diazo-1-imide.

The Isomeric Phenyl-1 : 2-*diazoiminonaphthalenes.*

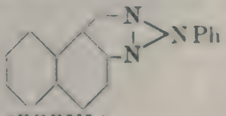
The foregoing experiments having shown that two isomeric diazoimines are possible corresponding with the formulæ XXXI and XXXII, an attempt was made to synthesise the latter from the



(XXXI.)



(XXXII.)



(XXXIII.)

base described by A. Harden as 1-phenyl-1 : 2-naphthylenediamine (*Ber.*, 1886, **19**, 343; *Annalen*, 1889, **255**, 161). The product obtained by this author's process did not correspond in composition with this diamine, and it was not affected by nitrous acid or amyl nitrite.

The isomeride (XXXI) has already been described by Zincke and Campbell (*Annalen*, 1889, **255**, 344); it was prepared for purposes of comparison by adding 20 per cent. aqueous sodium nitrite to a glacial acetic acid solution of the purified hydrochloride of 2-phenyl-1:2-naphthylenediamine (m. p. 138—140°). After repeated crystallisation from benzene, the colourless product melted at 143—144°. (Found, C=78·09; H=4·76; N=16·67. Calc., C=78·36; H=4·40; N=17·14 per cent.)

During the course of this investigation, Noelting, Grandmougin, and Freimann (*Ber.*, 1909, **42**, 1377) have given the formula XXXII to a diazoimine obtained as a by-product in the reduction of benzene-2-azo-α-naphthyl benzoate and the alkyl ethers of benzene-2-azo-α-naphthol. This mode of formation does not, however, afford definite evidence of the constitution of the diazoimine.

In addition to these diazoimines (XXXI and XXXII), a third isomeric triazole (XXXIII) was formerly obtained by Zincke and Lawson, who prepared it by oxidising benzeneazo-β-naphthylamine (*Ber.*, 1885, **18**, 798 and 3132). The relationship of these isomeric triazoles is still under investigation (Proc., 1910, **26**, 151).

The authors desire to express their thanks to the Research Grant Committees of the Royal Society and Chemical Society for grants which have partly defrayed the expenses of this investigation.

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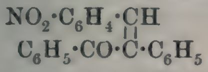
CLXXXII.—*Action of Light on the Stereoisomeric Piperonylideneacetones and on other Unsaturated Ketones.*

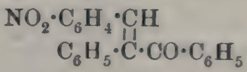
By Hans Stobbe and Forsyth James Wilson.

In a recent paper (*Annalen*, 1910, **374**, 237) we have shown that isomeric ketones of the type of benzylidenedeoxybenzoin, Ar·CH:CPh·COPh, can be converted into one another by heating them to their melting points and above, by the action of traces of hydrochloric acid, or by the action of sunlight on their benzene solutions in presence of iodine. These transformations lead to a state of equilibrium which, for example, in the case of the two stereoisomeric *o*-nitrobenzylidenedeoxybenzoins A and B:



$$\begin{array}{r} NO_2\cdot C_6H_4\cdot CH \\ \| \\ C_6H_5\cdot CO\cdot C\cdot C_6H_5 \end{array}$$

and



$$\begin{array}{l} NO_2\cdot C_6H_4\cdot CH \\ \qquad\quad\ \| \\ \qquad C_6H_5\cdot C\cdot CO\cdot C_6H_5 \end{array}$$

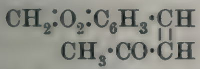
can be represented by the scheme:

$$\underset{\text{Dark yellow.}}{\text{Ketone A}} \rightleftarrows \underset{\text{Light yellow.}}{\textit{iso}\text{Ketone B.}}$$

The equilibrium for the three isomeric yellow *p*-nitrobenzylidenedeoxybenzoins A, B, and C can be illustrated diagrammatically as follows:

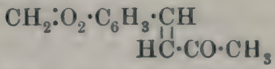
$$\begin{tikzcd} & \text{A} \arrow[dl, shift right] \arrow[dr, shift left] & \\ (\textit{iso}\text{Ketone})\ \text{B} \arrow[ur, shift right] \arrow[rr, shift left] & & \text{C}\ (\textit{allo}\text{Ketone}) \arrow[ul, shift left] \arrow[ll, shift left] \end{tikzcd}$$

On account of these results, we thought it advisable to study, on these lines, other unsaturated ketones of the benzylideneacetone and benzylideneacetophenone series. The ketones first investigated were the two stereoisomeric piperonylideneacetones:



$$\begin{array}{r} CH_2{:}O_2{:}C_6H_3\cdot CH \\ \| \\ CH_3\cdot CO\cdot CH \end{array}$$

and



$$\begin{array}{l} CH_2{:}O_2\cdot C_6H_3\cdot CH \\ \qquad\qquad\quad\ \| \\ \qquad\qquad HC\cdot CO\cdot CH_3 \end{array}$$

which were first prepared by Haber (*Ber.*, 1891, **24**, 618). We designate them with the letters A and B. The ketone A, obtained synthetically from piperonal and acetone, is yellow, and melts at 107°; the *iso*ketone B (m. p. 111°), obtained from A by crystallisation from a quantity of boiling water insufficient to dissolve it entirely, is white. While therefore under these conditions (at about 100°) the yellow ketone A is converted into the white ketone B, the *iso*ketone B is transformed, as Haber has already shown, into the ketone A by heating to 190°.

The following experiments were made in order to ascertain how the two ketones behave towards light.

Experiment I.—A solution of the yellow piperonylideneacetone (4 grams) in a solution of iodine in benzene (0·1 gram of iodine in 100 grams of benzene) was exposed to the action of direct sunlight for five weeks in March and April; it gradually became darker in colour. After shaking with sodium thiosulphate solution to remove the iodine, and evaporation, a dark mass was obtained which, after recrystallisation from alcohol in the presence of animal charcoal, yielded, in addition to much unaltered ketone A, only 0·7 gram of the white *iso*ketone B.

Experiment II.—A solution of the white *iso*ketone B (1·2 grams) in a 0·1 per cent. solution of iodine in chloroform was exposed to the action of direct sunlight. After a week's exposure in summer, the solution was worked up as in experiment I; the product consisted almost exclusively of the yellow ketone A, besides a very small amount of unaltered *iso*ketone B.

These experiments show that the two isomeric ketones, like the ketones of the benzylidenedeoxybenzoin type, are interconvertible —that light influences the two reciprocal processes indicated by the scheme:

$$\underset{\text{Yellow.}}{\text{Piperonylideneacetone (A)}} \rightleftarrows \underset{\text{White.}}{\text{Piperonylideneacetone (B)}}$$

Even if as yet these experiments have not been carried out under similar conditions,* and conclusions as to the state of equilibrium cannot yet be drawn, nevertheless the deeper coloured ketone A appears to be more stable when in the molten state than the white *iso*ketone B, and also to be more stable in solution towards light.

Other unsaturated ketones, anisylideneacetone, piperonylideneacetophenone, anisylideneacetophenone, and *o-methoxybenzylideneacetophenone*,† could not be converted into their hitherto unknown stereoisomerides either by a five weeks' exposure of their iodine-benzene solutions to direct sunlight, or by boiling these solutions for twelve hours in diffused daylight. In all these experiments the substances were for the most part recovered unaltered, and to a smaller extent they were converted into yellow, red, or brown resins, from which homogeneous products could not be obtained. These ketones therefore are probably stable towards sunlight, and could perhaps be converted into their labile stereoisomerides only by light of a different wave-length, for example, by ultra-violet rays (compare Störmer, *Ber.*, 1909, **42**, 4865). We intend to carry out these experiments in suitable solutions, and hope to communicate the results later.

Doubly unsaturated ketones, for example, cinnamylideneacetophenone, $C_6H_5\cdot CH{:}CH\cdot CH{:}CH\cdot CO\cdot C_6H_5$, behave quite differently from the simple unsaturated ones. This ketone is converted by the action of sunlight, not only into a stereoisomeride, but also into a polymeric ketone. An account of these investigations will be published shortly by H. Stobbe and Konrad Rücker.

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* In one experiment, when the *iso*ketone B in iodine-benzene solution was exposed to sunlight for a week during summer, the only product obtained was a resin.

† *o-Methoxybenzylideneacetophenone*, $C_6H_4(OMe)\cdot CH{:}CH\cdot COPh$, was prepared by condensing *o*-methoxybenzaldehyde (15 grams) and acetophenone (13·3 grams) in 70 grams of alcohol and 20 grams of sodium hydroxide solution (10 per cent.). It separates from the solution as an oil which soon solidifies, especially on rubbing, and a further amount (bringing the yield to 80—90 per cent. of the theoretical) can be obtained by adding water to the solution. It crystallises from light petroleum in pale yellow, felted needles, which melt at 58—59°:

0·1205 gave 0·3558 CO_2 and 0·0687 H_2O. C = 80·52; H = 6·33.

$C_{16}H_{14}O_2$ requires C = 80·67; H = 5·88 per cent.

The substance is readily soluble in alcohol, ether, or benzene.

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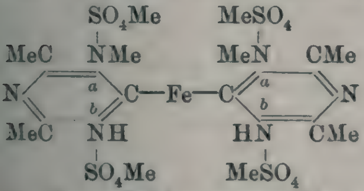
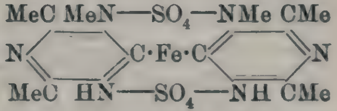
CLXXXIII.—*Tetramethyl Ferrocyanide and some Derivatives.*

By ERNALD GEORGE JUSTINIAN HARTLEY.

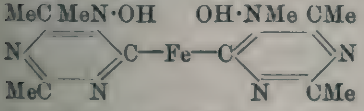
IN a recent communication (this vol., p. 1066) the author showed that methyl sulphate reacts with dry potassium ferrocyanide, and two salts (I) and (II) * were obtained of a hypothetical base (III), which was itself too unstable to be isolated:



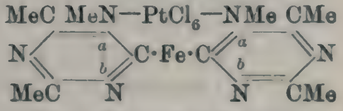
(I.) Hexamethyl ferrocyanogen dihydrogen methyl sulphate.



(II.) Hexamethyl ferrocyanogen dihydrogen sulphate.



(III.) Hypothetical Base.



(IV.) Hexamethyl ferrocyanogen platinichloride.

In these compounds two pairs of nitrogen atoms exhibit basic functions, but of an extremely weak nature in the case of that pair (*b*, *b*) which are not directly attached to methyl groups. Consequently the salts (I) and (II) give a strongly acid reaction in aqueous solution, whilst in the platinichloride (IV), which is formed from either of them, only the more basic pair (*a*, *a*) is combined with the acid radicle.

It was considered probable that the acid groups $MeHSO_4$ in (I), which are attached to the less basic pair of nitrogen atoms (*b*, *b*), were produced by moisture absorbed by the methyl sulphate mainly during filtration, when a hot-water funnel was used.

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* These formulæ are only put forward provisionally, as the constitution of the ferrocyanogen radicle is still uncertain. They are, however, in this case, very serviceable for representing the relationship between the various substances described.

Further experiments have since been made, in which greater care was taken to avoid the introduction of water vapour, when the reaction followed a somewhat different course and other products were isolated, but the complete account of their formation is still somewhat obscure.

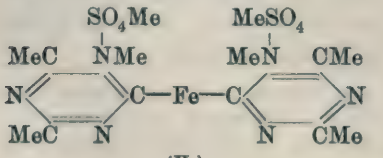
In order to ensure the absence of moisture in the materials used, the potassium ferrocyanide (20 grams), freshly precipitated from aqueous solution by means of alcohol for each experiment, was heated to 105° for forty-eight hours, and the methyl sulphate (150 c.c.) was distilled under diminished pressure just before use.

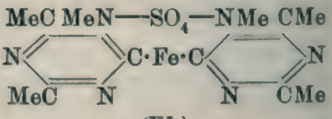
The reaction was accompanied by rather marked changes of colour, the mixture turning bright yellow after about one hour's heating, and then becoming purple. At the end of five hours the liquid was filtered, taking care to prevent it from coming in contact with moisture from the air. On cooling, a crop of purple crystals (about 3 grams) was deposited, which differed from those previously obtained at the same stage in the reaction (described as B, *loc. cit.*, p. 1068) in being soluble in ethyl alcohol and giving no precipitate with barium chloride. They were recrystallised from ethyl alcohol, when they lost a great part of the colouring matter (which appears to be of the nature of Prussian blue). This substance undergoes no change when kept in an exhausted desiccator over sulphuric acid; it is extremely hygroscopic, and forms a neutral solution in water, which gives the same platinichloride as (I) and (II). When dissolved in ethyl alcohol and treated with concentrated sulphuric acid, the acid sulphate (II) is precipitated. It is evidently therefore a salt of the base (III), and the analytical numbers show it to be the methyl sulphate, as was anticipated from its mode of formation:

0·2782 gave 0·0437 Fe_2O_3. Fe = 11·00.
0·2512 „ 0·2942 CO_2 and 0·1059 H_2O. C = 31·96; H = 4·71.
0·3272 „ 0·0504 Fe_2O_3. Fe = 10·78.

The second determination of iron was made with material crystallised a second time from alcohol and quite colourless.

These numbers correspond with the formula $C_{14}H_{24}O_8N_6S_2Fe$, or $(CH_3)_6FeC_6N_6(CH_3\cdot SO_4)_2$, which requires C = 32·04, H = 4·61, Fe = 10·68 per cent. Applying the same nomenclature as before, this would be called hexamethyl ferrocyanogen methyl sulphate, and may be represented by (V):


(V.)


(VI.)

The methyl sulphate solution, from which the above crystals had been removed, was then subjected to distillation under diminished pressure. There was at first a slight evolution of gas, which, however, soon ceased, after which the distillation was continued until no more liquid passed over, the final temperature being varied in different experiments from 80° to 130°. The residue (about 18 grams) in each case contained a portion which was almost insoluble in ethyl alcohol, and proved on analysis to be identical with (II); it differed in quantity, but was usually about one-third of the total weight of residue. The other portion was soluble in alcohol, and was deposited on evaporating the solution in slightly purple crystals always contaminated with some of (II), from which it could be freed by a second crystallisation. These crystals resembled the substance (V) in being extremely hygroscopic, neutral to litmus in aqueous solution, and in giving the same platinichloride (IV) and acid sulphate (II) under similar conditions. With barium chloride they gave no precipitate. In some cases they separated with alcohol of crystallisation, which was only very slowly given off in a vacuum. It was then found better for analytical purposes to redissolve in alcohol and precipitate with ether, when they were obtained as a fine, crystalline powder free from combined alcohol. They lose practically no weight at 100° in a vacuum, but when heated to this temperature in an ordinary air-bath they are hydrolysed by the moisture in the air and converted completely into (II), the presence of two SO_4 groups in the molecule being thereby proved.

The analytical numbers were as follows:

1. Substance twice crystallised from ethyl alcohol:

0·2196 gave 0·0324 Fe_2O_3. Fe = 10·33.

0·1803 ,, 0·2218 CO_2 and 0·0812 H_2O. C = 33·57; H = 5·04.

2. Substance crystallised once from ethyl alcohol and afterwards redissolved and precipitated with ether:

0·2839 gave 0·0418 Fe_2O_3. Fe = 10·31.

0·1266 ,, 0·1575 CO_2 and 0·0569 H_2O. C = 33·95; H = 5·03.

These numbers, together with the chemical properties of the substance, point to its being a mixture of the methyl and ethyl sulphates of the base (III).

The methyl sulphate, $(CH_3)_6FeC_6N_6(CH_3\cdot SO_4)_2$, requires C = 32·04, H = 4·61, Fe = 10·18; and the ethyl sulphate,

$$(CH_3)_6FeC_6N_6(C_2H_5SO_4)_2,$$

requires C = 34·77, H = 5·10, Fe = 10·14 per cent.

It is somewhat difficult to explain the presence of the ethyl groups. An examination of the methyl sulphate used, both by a combustion and by an analysis of the potassium salt ($KMeSO_4$)

produced by hydrolysis with alcoholic potash, gave no indication of the presence of a substance with a higher percentage of carbon or hydrogen. It seems more likely to be the result of a slight decomposition of the methyl sulphate during the long heating which the process requires, similar to that which takes place when this ester is distilled under atmospheric pressure. The products of this decomposition are presumably ethylene and sulphuric acid or methylsulphuric acid, and a partial recombination of the two former would result in the formation of some ethylsulphuric acid.

The production of some sulphuric acid in this way would also account for the considerable proportion of (II) always found, which in this case can hardly be due to the introduction of moisture during the experiment.

In consequence of the ease with which both the methyl sulphate (V) and the supposed mixture of methyl and ethyl sulphate can be quantitatively converted into the readily purified acid sulphate (II) by precipitation with sulphuric acid in alcoholic solution, and especially as this latter has proved to be the best starting point for additional derivatives, it was considered a waste of time to make further experiments with a view to separating the mixture into its constituents.

It was shown in the previous paper that the substance (I) is very readily converted into (II) by the loss of two molecules of methyl sulphate, this transformation taking place either by heating or even at the ordinary temperature on keeping for some days in an exhausted desiccator over sulphuric acid.

It might be expected that the neutral methyl sulphate (V) would behave in a similar manner, and by the loss of one molecule of methyl sulphate becomes a sulphate as represented by (VI), but this does not appear to be the case, since no trace of the latter compound is found amongst the products of the reaction just described, even when a temperature of 130° was reached, and there is no loss of weight when the pure salt (V) is kept in a vacuum.

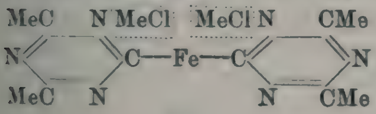
Although the sulphate (VI) is not formed from (V) as was expected, it can be prepared from (II) as follows. When baryta is added to an aqueous solution of the latter until the liquid is just neutral to litmus, the H_2SO_4 group is eliminated. On filtering from barium sulphate and evaporating to dryness in a vacuum over sulphuric acid, a white, extremely hygroscopic solid is left, which differs from the original salt in being readily soluble in ethyl alcohol, from which it separates in cubes apparently containing alcohol of crystallisation, since, on keeping for only a short time over sulphuric acid in an exhausted desiccator, they become opaque and fall to a white powder. The substance is quite neutral in aqueous solution, but is very unstable, soon turning yellow and decomposing, even when kept in a desiccator, and it is extremely difficult to obtain it in a suitable condition for analysis. When it has acquired a constant weight in a vacuum it still apparently retains about one molecule of alcohol, which it loses on heating with a certain amount of decomposition.

A determination of Fe and SO_4, with material dried to a constant weight in a vacuum, gave the following numbers:

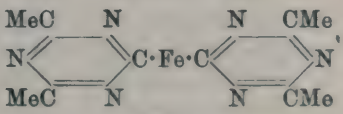
0·2196 gave 0·0417 Fe_2O_3. Fe = 13·29.
0·2646 „ 0·1337 $BaSO_4$. SO_4 = 20·79.

The loss of weight at 100° was 9·83. Calculating the percentages of Fe and SO_4 from the weight of salt left after heating, this gives Fe = 14·74, SO_4 = 23·06. $C_{12}H_{18}O_4N_6SFe$ requires Fe = 14·06, SO_4 = 24·10 per cent. $C_{12}H_{18}O_4N_6SFe + C_2H_6O$ contains C_2H_6O = 10·36 per cent.

These figures, together with the fact that the substance gives the platinichloride (IV), may be regarded as sufficient evidence for the above constitution, and as the corresponding chloride is far more stable and readily obtained pure, it was not considered advisable to sacrifice material in the attempts to obtain the sulphate in a more favourable condition for analysis.



(VII.)



(VIII.)

The chloride (VII) is also prepared from (II) by neutralising with baryta as above, and then adding a slight excess of barium chloride, filtering, and evaporating in a vacuum, when a white, crystalline mass is left and is extracted with ethyl alcohol. On adding ether to the alcoholic solution, hexamethyl ferrocyanogen chloride (VII) is precipitated as a very bulky, white, crystalline precipitate. This is not nearly so hygroscopic as the sulphate, and does not appear to decompose at all on keeping:

0·3252 gave 0·2476 AgCl. Cl = 18·82.
0·5780 „ 0·1242 Fe_2O_3. Fe = 15·04.
$C_{12}H_{18}N_6Cl_2Fe$ requires Cl = 18·99. Fe = 15·00 per cent.

Preparation of Tetramethyl Ferrocyanide.

When the above chloride is heated under diminished pressure, a steady evolution of gas begins to take place at about 140°, and is completed at this temperature after two to three hours.

The gas was collected over mercury and tested; it burnt with a green flame, and a few drops of water shaken up in the tube in which the combustion had taken place were found to contain hydrochloric acid. The gas was therefore presumably methyl chloride.

The residue had scarcely altered in appearance from the original salt, and showed no signs of fusion; it had an odour resembling that of *iso*cyanides, which it lost on keeping for some time in a vacuum; it was free from chlorine, and was readily soluble in chloroform, alcohol, or water, and insoluble in ether or acetone.

It resembles tetraethyl ferrocyanide prepared from silver ferrocyanide and ethyl iodide in its solubility and in giving in aqueous solution a white precipitate with mercuric chloride, a reddish-purple colour with ferric chloride, and a yellow, microcrystalline precipitate with platinic chloride.

An analysis gave numbers showing it to be tetramethyl ferrocyanide:

0·2352 gave 0·0694 Fe_2O_3. Fe = 20·66.
0·2057 „ 0·3309 CO_2 and 0·0808 H_2O. C = 43·90; H = 4·39.
$C_{10}H_{12}N_6Fe$ requires Fe = 20·56; C = 44·09; H = 4·44 per cent.

Its formation is evidently due to the loss of the two molecules of methyl chloride (shown in (VII) enclosed by dotted lines).

In order to obtain it quite pure, the best procedure is to dissolve it in chloroform, when a rather dark-coloured solution is formed, owing to a slight amount of decomposition during the heating. On gradually adding ether, the colouring matter is first precipitated, and can be filtered off. The substance is afterwards thrown down by a further addition of ether as an almost colourless precipitate. By repeating the process it can be obtained quite colourless. It is then crystallised from chloroform, from which it separates in large, light yellow, transparent, rectangular plates, containing chloroform of crystallisation, which is given off fairly rapidly at the ordinary temperature, and completely at about 60° in a few hours. A determination of iron was made on some material purified in this way and heated to 65° until a constant weight was obtained, and afterwards to 105°, when there was no further loss. 0·2729 gave 0·0801 Fe_2O_3; Fe = 20·55. Calc., Fe = 20·56 per cent. Tetramethyl ferrocyanide crystallises from water in yellowish-white aggregates, which appear amorphous, but when magnified are seen to consist of fine needles.

On strongly heating, it decomposes without melting, giving off an alkaline vapour, and leaving a residue of pure ferric oxide.

The original object of this research was to prepare tetramethyl ferrocyanide, and to determine its molecular weight in aqueous solution in order to ascertain whether this agreed with the double formula which was found to represent best the properties of calcium ferrocyanide (*Phil. Trans.*, 1909, *A*, **209**, 319). For this purpose it is proposed to make a series of determinations of the osmotic pressure of its solutions when sufficient material is available.

In conclusion, I wish to express again my thanks to Lord Berkeley, to whom I am greatly indebted for placing at my disposal his laboratory and all the apparatus and materials for continuing this research, and for the interest he has taken in its progress.

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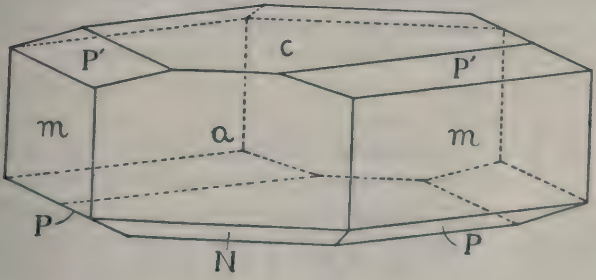
Appendix.

Mr. W. H. Barrett, of Balliol College, Oxford, kindly undertook an examination of the crystallographic properties of the acid sulphate (II). His description and measurements are herewith given as follows:

Small, yellow crystals from methyl alcohol, which soon begin to turn opaque. They can be obtained again transparent on recrystallisation from methyl alcohol. They are usually combinations of $a\{100\}$, $c\{001\}$, $m\{110\}$, and $N\{10\bar{1}\}$, and in habit either tabular parallel to $c\{001\}$, or elongated along the b axis, as in the drawing. On some crystals, forms $P\{\bar{1}12\}$ and $P'\{113\}$ were present, but on only one crystal were they sufficiently well developed to give measurable images of the goniometer signal. Nine crystals selected from two crops were measured, but many of the reflexions were too blurred to be of any value, and so the readings corresponding to these were discarded.



System: Monoclinic holosymmetric.

Habit: Tabular parallel to $c\{001\}$, or prisms elongated along the b axis.

Forms observed: $c\{001\}$, $a\{100\}$, $N\{10\bar{1}\}$, $m\{110\}$, $P\{\bar{1}12\}$, $P'\{113\}$.

Axial ratio: $a:b:c = 1{\cdot}9101 : 1 : 2{\cdot}0472$; $\beta = 93^\circ 1'$.

Table of Angles.

Measured angle.	No. of angles.	No. of crystals.	Limits.	Mean.	Calculated.
$a : \bar{c}$ (001) : ($\bar{1}$00)	14	8	92°49′—93° 8′	93° 1′	—
$c : N$ (001) : ($\bar{1}$01)	5	5	48 19 —48 48	48 36	—
$a : m$ (100) : (110)	23	8	62 16 —62 35	62 26	—
$c : P$ (001) : ($\bar{1}$12)	4	1	49 41 —49 52	49 46	49°54
$c : P'$ (001) : (113)	1	1	47°13′	47 13	46 50

Optical properties: The acute bisectrix coincides with the *b* axis; and the plane of the optic axes lies in the obtuse angle β, and is inclined to the *a* axis at an angle of about 30°, as shown by the extinction on a plate ground approximately parallel to (010). The optic axial angle is rather small, and the axes have a slight dispersion in the sense $s > v$. The crystal was too brittle to allow of making a section sufficiently thin to enable the sign of the birefringence or any dispersion of the bisectrices to be determined, but compensation of a crystal viewed through $c\{001\}$ shows that the birefringence must be positive.

The behaviour of the crystals in turning opaque is peculiar. The opacity starts from the two *c* faces, and, viewed through the *a* face, the opaque part resembles in form two pyramids whose summits gradually interpenetrate, and whose bases are the *c* faces. The opaque part has thus somewhat of an hour-glass shape.

CLXXXIV.—*The Relation of Position Isomerism to Optical Activity. Part VIII. The Rotation of the Menthyl Esters of the Alkyloxy- and Alkylamino-derivatives of Benzoic Acid.*

By Julius Berend Cohen and Harold Ward Dudley.

In previous investigations on this subject (Trans., 1903, **83**, 1214; 1904, **85**, 1262, 1271; 1905, **87**, 1190; 1906, **89**, 49, 460, 1479) the active esters submitted to optical examination included halogen, nitro- and nitro-halogen derivatives of benzoic acid. The results derived from the study of nine separate series of compounds clearly indicated that, with the single exception of the ortho-isomeride of the iodobenzoic esters,* the ortho-substituent had the greatest influence in diminishing the rotation, as in the halogen derivatives, or in increasing it, as in the nitro-compounds, and that substituents in the meta- and especially in the para-position had a very subordinate effect. In the following table we have limited ourselves to reproducing the four series of mono-derivatives of the benzoic esters, as the presence of two substituents bears a close relation to that of the single atom or group:

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* We propose to study the effect of temperature on the rotation of the three isomeric iodobenzoic esters.

	$[M]_D^{20°}$.			$[M]_D^{65°}$.
Menthyl ester.	Cl.	Br.	I.	NO_2.
Ortho....................	−195·0°	−205·5°	−246·0°	−381·0°
Meta	237·0	238·5	234·5	251·0
Para	237·5	237·0	241·0	235·0

Menthyl benzoate, $[M]_D^{20}$ −239°.

Positive Groups.—It will be observed that the compounds examined contain only negative substituents. The only observations on active esters of benzoic acid containing positive groups are those of Tschugaeff (*Ber.*, 1898, **31**, 1775), who examined the menthyl esters of the three toluic acids, to which the following values are assigned:

Ortho, $[M]_D^{20}$ −231·2° Meta, $[M]_D^{20}$ −270·8° Para, $[M]_D^{20}$ −252·4°

Here the order of rotation is the reverse of that given above; for although the value of the ortho-compound is rather less than that of menthyl benzoate, that of the para-compound is much higher.

We have repeated these observations at 20° and 100° with carefully prepared specimens of the three esters. They were examined both before and after distillation. Distillation under diminished pressure produced no measurable change in rotation.

The values for the ortho- and meta-compounds are practically the same as those obtained by Tschugaeff, but that of the para-compound is much below his number. The previous order remains nevertheless unaltered:

Menthyl ester.	$[M]_D^{20°}$.	$[M]_D^{100°}$.
Ortho	−231·0°	−223·0°
Meta	240·0	234·5
Para	246·5	237·0

Effect of Temperature.—An interesting feature in these observations is the effect produced on the rotation by rise of temperature. The relatively large decrease in the value of the para-compound at 100° brings the meta- and para-compounds within a few units of one another. This value at the higher temperature is especially noteworthy when compared with that of menthyl benzoate at the same temperature. In former comparisons with menthyl benzoate we have taken Tschugaeff's value, $[M]_D^{20}$ −236·3°;

but this was obtained in benzene solution, whereas, with very few exceptions, we have examined the fused substances without solvent. It seemed desirable to ascertain the value for fused menthyl benzoate. This has been effected first at 100°, and then by supercooling (the substance melts at 54°) at about 20°, with the following result:

	20°.	100°.
$[M]_D$	−239°	−233°

If now we compare the values of the menthyl toluates with that of menthyl benzoate at the higher temperature, the old order is reproduced, in which the rotation of the meta- and para-compounds approximates to that of the unsubstituted ester. The question of temperature obviously plays a very important rôle when instituting a comparison between the rotational values of a compound and its derivatives, a matter which demands more attention than it has so far received.

The number of observations on the effect of temperature on the rotation of fused substances is not very large. A list of most of them, references to which are given in the foot-note below,* has been collected by Walden (*Ber.*, 1905, **38**, 363, 382), who, without throwing any light on the cause of these changes, merely states "da der Temperaturcoëfficient abhängig ist von der Constitution der activen Substanz, so dürfte er in der Folge eine grössere Beachtung verdienen als bisher." Winther (*Zeitsch. physikal. Chem.*, 1906, **55**, 259) has found an empirical formula which gives values in close agreement with the observed results. But it is difficult to discover any apparent relation between temperature-coefficient and constitution in the different series, for even among isomeric compounds the value in the case of one isomeride may be positive with rise of temperature, in that of another, negative, and in a third it may fluctuate. As an illustration we may give the observations on the three menthyl nitrobenzoates (Cohen and Armes, Trans., 1905, **87**, 1190):

	$[M]_D$.		
t.	Ortho.	Meta.	Para.
100°	−370°	−250°	−230°
80	380	253	232
70	379	252	233
65	381	251	237·5
40	—	251	—
20	—	252	—

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* Frankland and Wharton, Trans., 1896, **69**, 1587; Frankland and Patterson, *ibid.*, 1898, **73**, 199; Frankland and McCrae, *ibid.*, 1898, **73**, 307; Patterson and McCrae, *ibid.*, 1900, **77**, 1107; Patterson, *ibid.*, 1904, **85**, 765, 1133; Patterson and Taylor, *ibid.*, 1905, **87**, 34; Patterson and Kaye, *ibid.*, 1906, **89**, 1884; 1907, **91**, 708; Winther, *Zeitsch. physikal. Chem.*, 1903, **45**, 331; 1906, **55**, 259; **56**, 703; 1907 **60**, 566, 590; Walden, *Ber.*, 1905, **38**, 363.

The temperature-coefficients in the case of the ortho- and para-compounds are negative, whilst in that of the meta-compound it fluctuates. The values in all cases are small. But when we turn to the alkyloxy-esters, we find that the effect of temperature is very marked, as may be seen from the following table:

	$[M]_D^{20°}$.			$[M]_D^{100°}$.		
Menthyl ester.	*o.*	*m.*	*p.*	*o.*	*m.*	*p.*
Methoxybenzoic acid......	−148·0°	−247·5°	−250·5°	−155·0°	−242·5°	−238·5°
Ethoxybenzoic ,, ...	solid	244·0	solid	157·5	237·5	238·5
Propoxybenzoic ,, ...	170·5	240·5	250·0	180·0	235·0	234·0
*iso*Propoxybenzoic acid...	169·0	—	246 0	176·0	—	233·5
*iso*Amyloxybenzoic ,, ...	187·0	240·5	247·5	196·0	237·5	234·0
Allyloxybenzoic ,, ...	solid	—	252·0	175·0	—	237·0
Benzyloxybenzoic ,, ...	168·5	—	255·0	159·0	—	239·0
Methoxynaphthoic ,, ...	(β)166·5	—	(α) 266·0	(β) 159·0	—	(α) 239·0

Menthyl benzoate, $[M]_D^{20}$ −239°, $[M]_D^{100}$ −233°.

Whilst the temperature-coefficients of the ortho-compounds are small, and for the most part positive with rise of temperature, those of the para-compounds are large and negative, whilst those of the meta- are the smallest of the three and negative. The general result is that at the higher temperature the rotational values of the meta- and para-compounds approximate, like those of the toluic esters, to the value of menthyl benzoate. It appears therefore that in comparing the activity of position isomerides, two factors have to be considered, namely, the change in rotation due to structure, and that produced by the physical condition of the compounds under examination. The question then arises; which is to be regarded as the standard temperature? If we take the higher temperature, the rule which is applicable to the esters with negative substituents holds equally in the case of those with positive groups, that is to say, the ortho-substituent has the greatest influence, and the meta- and para-substituents a very subordinate effect.*

If, according to Winther (*loc. cit.*), change of rotation in a compound is conditioned by change in internal pressure, it seems probable that a temperature widely removed from the crystallising point, and therefore from the region in which molecular aggregates may be formed, will afford a more correct basis for comparison.

It is for this reason that provisionally we are disposed to regard the values at 100° as the more satisfactory for the purpose of comparison until more light has been thrown on this aspect of the problem. Another fact in support of our view of the influence of contiguous groups on the rotational value of the active group, is that furnished by menthyl phenylacetate. This substance, which is isomeric with the menthyl toluates, exhibits both in its mobile character (the toluates are very viscid liquids) as well as in its rotation a much closer resemblance to the aliphatic than to the aromatic esters (Rupe, *Annalen*, 1909, **369**, 311, 927):

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* The rule laid down by Frankland and Wharton (Trans., 1896, **69**, 1309, 1583), in which the para-isomeride is supposed to exert the greatest effect, is not only contradicted by some of their own and others observations, but seems quite incapable of proof where solvents are used, owing to the indeterminate influence of the solvent.

	$[M]_D^{20^\circ}$.
Menthyl *o*-toluate	−231·0°
,, *m*-toluate	240·0
,, *p*-toluate	246·5

	$[M]_D^{20^\circ}$.
Menthyl phenylacetate ..	−188°
,, propionate	160
,, butyrate	160

Dimethylaminobenzoic Esters.—The ortho- and para-esters were obtained in the form of viscid liquids of a red colour, which could neither be crystallised nor distilled without decomposition. The only criterion of purity was the analysis, the fact that the acid chloride of *p*-dimethylaminobenzoic acid yielded with methyl alcohol the pure methyl ester (m. p. 102°), and that the menthyl ester was unchanged in composition and in rotation after precipitation from solution in light petroleum as the hydrochloride. Seeing that the acid chlorides have a deep orange colour, and the menthyl esters retain the red colour after reprecipitation as hydrochlorides, we are inclined to think that the colour is the natural physical attribute of these esters, although by analogy we should have anticipated a different result, the acids themselves being quite colourless.

Owing to the very viscid nature of the esters, it was difficult to ascertain their densities at 20°, and the rotations have only been determined at 100°:

	$[M]_D^{100^\circ}$.
Menthyl ortho-dimethylaminobenzoate	−101°
,, para-dimethylaminobenzoate	258

Assuming that these values represent an approximation to the true values of the pure substances, the result is interesting, for although the rotation of the para-compound is about 20° higher than the mean of the other para-compounds, the difference produced by the dimethylamino-group in the ortho-position is nearly treble this amount.

For convenience of reference, the following table of densities and specific and molecular rotations at 20° and 100° are collected together.

Menthyl ester.	d_4^{20}.	d_4^{100}.	$[\alpha]_D^{20^\circ}$.	$[\alpha]_D^{100^\circ}$.	$[M]_D^{20^\circ}$.	$[M]_D^{100^\circ}$.
o-Methoxybenzoic ester......	1·045	0·9823	−51·08°	−53·37°	−148·2°	−154·7°
m-Methoxybenzoic ,, ...	1·034	0·9766	85·39	83·69	247·6	242·7
p-Methoxybenzoic ,, ...	1·036	0·9766	86·47	82·30	250·7	238·6
o-Ethoxybenzoic ,, ...	solid	0·9641	—	51·75	—	157·3
m-Ethoxybenzoic ,, ...	1·017	0·9582	80 26	78·10	244 0	237·4
p-Ethoxybenzoic ,, ...	solid	0·9622	—	78·39	—	238·3
o-Propoxybenzoic ,, ...	1·019	0·9589	53 59	56·63	170·4	180·1
m-Propoxybenzoic ,, ...	1·010	0·9511	75·65	73·93	240·6	235·1
p-Propoxybenzoic ,, ...	1·016	0·9569	78·66	73·60	250·1	234·0
o-*iso*Propoxybenzoic ester...	1·034	0·9766	53·08	56·54	168·8	175·7
p-*iso*Propoxybenzoic ,, ...	1·011	0·9514	77·42	73·37	246·1	233·3
o-*iso*Amyloxybenzoic ,, ...	1·003	0·9442	54·01	56 69	186·8	196·2
m-*iso*Amyloxybenzoic ,, ...	0·9947	0·9363	69·53	68·66	240·6	237·6
p-*iso*Amyloxybenzoic ,, ...	0·9954	0·9400	71·57	67·57	247·6	233·8
o-Allyloxybenzoic ester......	solid	0·9689	—	55·35	—	174·9
p-Allyloxybenzoic ,, ...	1·027	0·9689	79·69	74·95	251·8	236·9
o-Benzyloxybenzoic ester:						
(PCl_5)	1·147	1·089	44·89	42·28	164·3	154·7
($SOCl_2$)	1·142	1·083	47·07	44·49	172·3	162·8
p-Benzyloxybenzoic ester ...	1·064	1·0015	69·68	65 29	255·1	238·9
o-Dimethylaminobenzoic ester	—	1·019	—	33 29	—	100·9
p-Dimethylaminobenzoic ester	—	0·9852	—	85·13	—	257·9
α-Methoxynaphthoic ester...	1·076	1·022	78·27	70·32	266 2	239·0
β-Methoxynaphthoic ,, ...	1·083	1·025	48·94	46·84	166·4	159·2
β-Benzyloxynaphthoic ester	1·118	1·058	87·27	77·82	363·0	324·4
o-Toluic ester	0·9982	0·9383	84·35	81·41	231·1	223·1
m-Toluic ,, ...	0·9946	0·9352	87·59	85·63	240·0	234·7
p-Toluic ,, ...	0·9937	0·9336	89·93	86·56	246·4	237·2
Phenylacetic ester	1·002	0·9400	68·70	65·56	188·2	179·6
Benzoic ester	1·002	0·9417	91·95	89·47	239·0	232·7

Melting Points of the Acids.—The melting points of the alkyloxybenzoic acids which have been ascertained in the course of this investigation are collected in the following table:

Acid.	Methoxy.	Ethoxy.	Propoxy.	*iso*Propoxy.	*iso*-Amyloxy.	Allyloxy.	Benzyloxy.
Ortho	99—101°	19— 20°	low m. p.	liquid	liquid	60— 62°	76— 77°
Meta	104—105	137	71— 72°	—	74— 75°	—	—
Para	180—182	195—196	145—147	160—163°	141—142	160—162	188—190°

It will be seen that the melting point rises from the ortho- to the para-compound. This is quite in accordance with other observations on the melting points of the three position isomerides. For example, the three series of halogen benzoic acids exhibit a similar relationship:

Acid.	Chlorobenzoic.	Bromobenzoic.	Iodobenzoic.
Ortho..............	137°	148°	162°
Meta	152	155	188
Para	236	251	265

Melting Points of the Menthyl Esters.—There is very little regularity to be observed in the melting points of the menthyl esters. They are for the most part viscid liquids of low melting point, and their viscid character when fused is probably accountable for the fact that many of them do not crystallise readily, and that a few have not yet been obtained in the solid form:

Menthyl ester.	Methoxy.	Ethoxy.	Propoxy.	*iso*Amyloxy.	Allyloxy.
Ortho	42°	52—53°	40—41°	liquid	61—62°
Para	liquid	76—77	34—35	54—55°	liquid

Reaction Temperature of the Acid Chloride and Menthol.—In the course of preparing the menthyl esters by heating the acid chloride with menthol, we have taken occasion to note approximately the temperature at which the reaction appeared to begin. This was done by observing the first appearance of bubbles of hydrogen chloride in the liquid. Although the reaction temperatures cannot be regarded as very accurate, the results seem to us to possess a certain interest, on account of the uniformly lower temperature at which the ortho-compound reacts. This is exactly the reverse of the behaviour of the ortho-halogen and nitro-compounds, which require a higher temperature to bring about combination (Cohen, Trans., 1906, **89**, 1482). Seeing that the unsubstituted benzoyl chloride requires a temperature of 88° to initiate the reaction with menthol, it is clear that the alkyloxy-group in the ortho-position facilitates combination. These observations have a direct bearing on the subject of steric hindrance, and furnish another example of the fact that the nature rather than the position of a particular group adjoining the reacting group determines the character of the process (Cohen and McCandlish, Trans., 1905, **87**, 1261):

Acid chloride.	Ortho.	Meta.	Para.
Toluoyl chloride	68°	97°	78°
Methoxybenzoyl chloride	60	90	100
Ethoxybenzoyl ,,	37	70	130
Propoxybenzoyl ,,	48	100	79
*iso*Propoxybenzoyl ,,	60	—	78
*iso*Amyloxybenzoyl ,,	66	93	105
Allyloxybenzoyl ,,	57	—	85
Benzyloxybenzoyl ,,	75	—	100
Methoxynaphthoyl ,,	(α) 87	(β) 85	—
Benzoylnaphthoyl ,,	88	—	—

EXPERIMENTAL.

The general method for preparing the alkyloxy-esters of menthol was to convert the hydroxy-acid into the methyl ester, and act on this with sodium methoxide and the alkyl iodide in alcoholic solution. The alkyloxy-ester was then hydrolysed with aqueous or alcoholic sodium hydroxide or potassium hydroxide, and the acid separated. The alkyloxy-acid was next converted into the acid chloride by means of phosphorus pentachloride, or in a few cases by thionyl chloride, and the resulting acid chloride heated with menthol. The excess of menthol was then removed by distillation in steam, and the product extracted with ether, shaken with sodium carbonate to remove free acid, and the menthyl ester finally separated. In the case of the meta- and para-methoxy- and ethoxy-acids, it was possible to convert the hydroxy-acids directly into these compounds by employing methyl and ethyl sulphate; but the latter do not react at all with the ortho-hydroxy-acids, nor with the α- and β-hydroxynaphthoic acids.

The preparation of the menthyl esters of ortho- and meta-methoxybenzoic acid are fully described by way of illustration, but in the subsequent preparations, which are mainly repetitions of the same process, only such details as the properties of the products and the yields are given.

The analyses are collected together in a table at the end.

Menthyl o-Methoxybenzoate, $C_6H_4(OMe)\cdot CO_2\cdot C_{10}H_{19}$. — Thirty grams of methyl salicylate, 4·5 grams of sodium in 100 c.c. of methyl alcohol, and 30 grams of methyl iodide were heated in a flask with reflux condenser for several hours. The greater part of the alcohol was then removed on the water-bath and the residue poured into water, which was rendered alkaline with sodium hydroxide to dissolve unaltered methyl salicylate, and extracted with ether. The ethereal extract was dehydrated, the ether removed, and the residue distilled under diminished pressure. The methoxy-ester boils at 140—144°/15 mm.; yield 25 grams. It was hydrolysed with 100 c.c. 10 per cent. sodium hydroxide solution, giving 18 grams of acid melting at 99—101°. Twelve grams of the acid were heated with 16 grams of phosphorus pentachloride on the water-bath. The phosphoryl chloride was removed as far as possible on the water-bath under diminished pressure and in a current of dry air. Without distilling the residual acid chloride (13 grams), which partly decomposes even at a low pressure, it was heated with an equal weight of menthol. The reaction began at about 60°, and was completed by heating for two hours at 130°. The product, after distillation in steam to remove menthol, solidified, and was digested with sodium carbonate solution to remove free acid and filtered. The yield of crude product (m. p. 38—40°) was 22 grams. It was recrystallised from alcohol, and melted at 42°. Owing to its low melting point and tendency to superfusion, it is very difficult to crystallise from any solvent, and usually separates as an oil, remaining liquid for days, even when cooled in a freezing mixture.

The rotation of the ester in a 3·02-cm. tube was then determined, and it was then distilled under diminished pressure. It boiled at 222—226°/12 mm., the main portion distilling at 226°. On cooling, it solidified and melted at 38—40°. The rotation of the distillate was determined, and gave somewhat lower results.

The rotation of another specimen in which the acid chloride was distilled without decomposition, and which gave a rather purer product is entered in the last column:

	Before distillation.	After distillation.	Specimen II (undistilled).
α_D^{20}	$-15{\cdot}95°$	$-15{\cdot}10°$	$-16{\cdot}12°$
α_D^{100}	$15{\cdot}65$	$14{\cdot}90$	$15{\cdot}84$

Specimen II: $d_4^{20} = 1{\cdot}045$; $d_4^{100} = 0{\cdot}9823$; $l = 3{\cdot}02$ cm.
$[\alpha]_D^{20}$ $-51{\cdot}08°$; $[\alpha]_D^{100}$ $-53{\cdot}37°$.
$[M]_D^{20}$ $-148{\cdot}2°$; $[M]_D^{100}$ $-154{\cdot}7°$.

Menthyl m-*Methoxybenzoate.*—27·6 Grams of *m*-hydroxybenzoic acid, 200 c.c. of 10 per cent. sodium hydroxide solution, and 24 c.c. of methyl sulphate were boiled for two and a-half hours. The liquid was then cooled and extracted with ether to remove impurities. After removing the ether, the liquid was acidified with hydrochloric acid, which precipitated the acid. Twenty-one grams of acid were obtained, which, after recrystallisation from boiling water, melted at 104·5°. It was converted into the acid chloride, and, after careful removal of the phosphoryl chloride, was heated with menthol without previous distillation. The reaction began at about 90°, and proceeded slowly. After separation of the free menthol and acid, as described above, the ester was obtained as a viscid liquid with a pale yellow colour. It distilled at 236—237°/30 mm., and gave a colourless distillate. A second distilled specimen is entered in the last column:

	Before distillation.	After distillation.	Specimen II (distilled).
α_D^{20}	$-26{\cdot}70°$	$-26{\cdot}25°$	$-26{\cdot}58°$
α_D^{100}	$24{\cdot}70$	$24{\cdot}10$	—

Specimen I, before distillation: $d_4^{20} = 1{\cdot}034$; $d_4^{100} = 0{\cdot}9766$; $l = 3{\cdot}02$ cm.
$[\alpha]_D^{20}$ $-85{\cdot}39°$; $[\alpha]_D^{00}$ $-83{\cdot}69°$.
$[M]_D^{20}$ $-247{\cdot}6°$; $[M]_D^{100}$ $-242{\cdot}7°$.

Menthyl p-*Methoxybenzoate.*—The para-compound was prepared in exactly the same manner as the meta-compound. The methoxy-acid melts at 180—182°. The reaction between the acid chloride and menthol began a little above 100° and proceeded vigorously. Nine grams of acid gave 9·5 grams of acid chloride and 15 grams of crude ester. The ester resembles the meta-compound. It is a viscid liquid with a faint yellow colour, which boils at 229—230°/15 mm., and gives a colourless distillate. Another distilled specimen is entered in the last column:

	Before distillation.	After distillation.	Specimen II (distilled).
α_D^{20}	$27{\cdot}08°$	$27{\cdot}05°$	$26{\cdot}92°$
α_D^{100}	$24{\cdot}30$	$24{\cdot}27$	—

Specimen I: $d_4^{20} = 1·036$; $d_4^{100} = 0·9766$; $l = 3·02$ cm.
$[\alpha]_D^{20}$ − 86·47° ; $[\alpha]_D^{100}$ − 82·30°.
$[M]_D^{20}$ − 250·7° ; $[M]_D^{100}$ − 238·6°.

Menthyl o-*Ethoxybenzoate*, $C_6H_4(OEt){\cdot}CO_2{\cdot}C_{10}H_{19}$.—The ortho-ester was prepared in exactly the same manner as the corresponding methoxy-derivative, using ethyl iodide in place of methyl iodide. The colourless ethoxy-ester distilled at 180—185°/113 mm. The ethoxy-acid melts at 19—20°, but owing to its low melting point it is difficult to crystallise, and cannot be distilled undecomposed. It was therefore converted directly into the acid chloride. Sixty grams of salicylic ester gave the same weight of ethoxy-ester, from which 50 grams of ethoxy-acid were obtained. Seventeen grams of the acid gave 22 grams of acid chloride and 33 grams of crude ester. The reaction with menthol began at 37°, and was completed in two to three hours at 100°. The menthyl ester crystallises in colourless prisms from alcohol (m. p. 52—53°). It could not be supercooled to 20°. Two specimens were prepared, and the mean of the rotations taken for calculation.

	Specimen I.	Specimen II.
α_D^{100} ……………	15·00°	15·09°

Mean: $d_4^{100} = 0·9641$; $l = 3·02$ cm.
$[\alpha]_D^{100}$ − 51·75° ; $[M]_D^{100}$ − 157·3°.

Menthyl m-*Ethoxybenzoate*.—The ester was prepared in the same manner as the *m*-methoxy-ester, using ethyl sulphate in place of methyl sulphate. The acid melts at 137°. It was converted into the acid chloride, which distilled without decomposition at 135—140°/16 mm., and solidified on cooling. It crystallises from light petroleum in long prisms, melting at 27—28°. When heated with menthol the action began about 70°. After purification, the ester consisted of a pale yellow oil, which distilled undecomposed at 230°/18 mm. Fifteen grams of acid gave 14·5 grams of acid chloride and 22 grams of ester. Two specimens were prepared, and the mean of the rotations taken for calculation:

	Specimen I.	Specimen II.
α_D^{20} ……………	− 24·99°	− 24·33°
α_D^{100} ……………	22·92	22·28

Mean: $d_4^{20} = 1·017$; $d_4^{100} = 0·9582$; $l = 3·02$ cm.
$[\alpha]_D^{20}$ − 80·26° ; $[\alpha]_D^{100}$ − 78·10°.
$[M]_D^{20}$ − 244·0° ; $[M]_D^{100}$ − 237·4°.

Menthyl p-*Ethoxybenzoate*.—The ester was obtained in the same manner as the *m*-ethoxy-compound. The acid melted at 195—196°. The acid chloride is a colourless liquid, which distils undecomposed at 160°/20 mm. On heating with menthol, the action began at 130°, and the mixture was maintained at 140° for two hours. Twelve grams of acid gave 9 grams of acid chloride and 12 grams of ester.

The ester, after distillation in steam, solidified, and was recrystallised from alcohol (m. p. 76—77°). It distils undecomposed at 230—235°/16 mm. Two specimens were prepared, and gave the following rotations:

	Specimen I.	Specimen II.
α_D^{100}	$-22{\cdot}73°$	$-22{\cdot}83°$

Mean : $d_4^{100} = 0{\cdot}9622$; $l = 3{\cdot}02$ cm.
$[\alpha]_D^{100}$ $-78{\cdot}39°$; $[M]_D^{100}$ $-238{\cdot}3°$.

Menthyl o-*Propoxybenzoate*, $C_6H_4(O{\cdot}C_3H_7){\cdot}CO_2{\cdot}C_{10}H_{19}$. — The propoxy-methyl ester was obtained from methyl salicylate and propyl iodide in the usual way, and distilled at 157—163°/45 mm. After hydrolysis with 20 per cent. sodium hydroxide solution, the acid was precipitated as an oil of very low melting point, which could not be recrystallised, and was not further purified. It was converted directly into the acid chloride, which distilled at 147—155°/12—15 mm. The reaction with menthol began at 48°. The menthyl ester was obtained as a solid, which crystallised from methyl alcohol in lustrous leaflets, melting at 40—41°. Only one specimen was prepared:

α_D^{20} $-16{\cdot}50°$; α_D^{100} $-16{\cdot}40°$.
$d_4^{20} = 1{\cdot}019$; $d_4^{100} = 0{\cdot}9589$; $l = 3{\cdot}02$ cm.
$[\alpha]_D^{20}$ $-53{\cdot}5°$; $[\alpha]_D^{100}$ $-56{\cdot}63°$.
$[M]_D^{20}$ $-170{\cdot}4°$; $[M]_D^{100}$ $-180{\cdot}1°$.

Menthyl m-*Propoxybenzoate*.—Fifty grams of *m*-hydroxybenzoic acid were boiled with 150 c.c. of methyl alcohol and 10 c.c. of concentrated sulphuric acid, and yielded 46 grams of ester, melting at 68—70°. The ester was boiled with one equivalent of sodium in 170 c.c. of methyl alcohol, and one equivalent of propyl iodide. The crude ester weighed 55 grams, and distilled at 159—161°/15 mm., yielding 44 grams of pure, colourless product. The ester yielded 33 grams of acid, crystallising in long prisms, melting at 71—72°. The acid gave an equal weight of acid chloride, which distilled without decomposition at 155—160°/18 mm., and solidified on cooling. It melted at 26—28°. The action with menthol began at 100°. Sixteen grams of acid chloride gave 22 grams of ester, which distilled undecomposed at 235°/18 mm.:

α_D^{20} $-23{\cdot}09°$; α_D^{100} $-21{\cdot}23°$.
$d_4^{20} = 1{\cdot}010$; $d_4^{100} = 0{\cdot}9511$; $l = 3{\cdot}02$ cm.
$[\alpha]_D^{20}$ $-75{\cdot}65°$; $[\alpha]_D^{100}$ $-73{\cdot}93°$.
$[M]_D^{20}$ $-240{\cdot}6°$; $[M]_D^{100}$ $-235{\cdot}1°$.

Menthyl p-*Propoxybenzoate.*—Methyl *p*-propoxybenzoate was prepared in the usual way, and was obtained as a pale yellow oil, having a peculiar, garlic-like odour (b. p. 165—170°/40 mm.). It solidified on cooling, and melted at 15°. The acid obtained on hydrolysis crystallised from alcohol in colourless, glistening plates, melting at 145—147°. The acid chloride, which had a green colour, distilled at 145—150°/12 mm. The action with menthol began at 79°. The menthyl ester crystallised from methyl alcohol in tufts of colourless needles, melting at 34—35°:

$\alpha^{20}_{\mathrm{D}}\ -24\cdot12^\circ$; $\alpha^{100}_{\mathrm{D}}\ -21\cdot27^\circ$.
$d^{20}_{4}=1\cdot016$; $d^{100}_{4}=0\cdot9569$; $l=3\cdot02$ cm.
$[\alpha]^{20}_{\mathrm{D}}\ -78\cdot66^\circ$; $[\alpha]^{100}_{\mathrm{D}}\ -73\cdot60^\circ$.
$[\mathrm{M}]^{20}_{\mathrm{D}}\ -250\cdot1^\circ$; $[\mathrm{M}]^{100}_{\mathrm{D}}\ -234\cdot0^\circ$.

Menthyl o-iso*Propoxybenzoate.*—Methyl *o-iso*propoxybenzoate is a colourless oil, boiling at 140—145°/16 mm. Only 58 per cent. of the theoretical quantity of ester was obtained, part of the original methyl salicylate being hydrolysed in the process. The acid was obtained as an oil, which did not crystallise, nor could it be purified by conversion into a salt. It was therefore converted into the acid chloride without purification. The acid chloride was a brown liquid which could not be distilled. It was heated directly with menthol. The action began at 60°, and the menthyl ester obtained was a dark red, viscid liquid, which was only partly decolorised by animal charcoal. On attempting to distil the ester, a pale yellow and much more mobile liquid was collected at 205—212°/9 mm., but apparently some decomposition had occurred, as a dark residue remained in the distilling flask. Subsequent analysis showed that both the undistilled and distilled portions contained a small quantity of phosphorus. The dark colour of the acid chloride also pointed to a secondary action between the acid chloride and the phosphorus chloride or oxychloride, and two other preparations failed to give an ester free from phosphorus. The rotations of these specimens were higher than those of the other ortho-compounds, no doubt owing to the presence of phosphorus compound. The following observations were made with the distilled ester:

$\alpha^{20}_{\mathrm{D}}\ -16\cdot58^\circ$; $\alpha^{100}_{\mathrm{D}}\ -16\cdot29^\circ$.
$d^{20}_{4}=1\cdot034$; $d^{100}_{4}=0\cdot9766$; $l=3\cdot02$ cm.
$[\alpha]^{20}_{\mathrm{D}}\ -53\cdot08^\circ$; $[\alpha]^{100}_{\mathrm{D}}\ -56\cdot54^\circ$.
$[\mathrm{M}]^{20}_{\mathrm{D}}\ -168\cdot8^\circ$; $[\mathrm{M}]^{100}_{\mathrm{D}}\ -175\cdot7^\circ$.

Menthyl p-iso*Propoxybenzoate.*—Methyl *p-iso*propoxybenzoate is a colourless oil, boiling at 159—162°/15 mm. The yield was 70 per cent. of the theory. The *p*-propoxy-acid crystallised from spirit in colourless needles, melting at 160—163°. The acid chloride was best obtained by the action of phosphorus pentachloride in benzene solution. The reaction with menthol began about 78°. The ester crystallised from alcohol in colourless crystals, melting at 57—58°:

$\alpha^{20}_{\mathrm{D}}\ -23{\cdot}64^\circ;\ \alpha^{100}_{\mathrm{D}}\ -21{\cdot}08^\circ.$
$d^{20}_{4}=1{\cdot}011;\ d^{100}_{4}=0{\cdot}9514;\ l=3{\cdot}02$ cm.
$[\alpha]^{20}_{\mathrm{D}}\ -77{\cdot}42^\circ;\ [\alpha]^{100}_{\mathrm{D}}\ -73{\cdot}37^\circ.$
$[\mathrm{M}]^{20}_{\mathrm{D}}\ -246{\cdot}1^\circ;\ [\mathrm{M}]^{100}_{\mathrm{D}}\ -233{\cdot}3^\circ.$

Menthyl o-iso*Amyloxybenzoate*, $C_6H_4(O{\cdot}C_5H_{11}){\cdot}CO_2{\cdot}C_{10}H_{19}$.—Methyl *o-iso*amyloxybenzoate is a nearly colourless oil, boiling at 160—164°/14 mm., the yield being about 45 per cent. of the theory. The *iso*amyloxy-acid, which was obtained as an amber-coloured oil, was purified by recrystallisation of its calcium salt. The acid chloride was prepared with phosphorus pentachloride in benzene solution, and decomposes on distillation under diminished pressure. The reaction with menthol began at 66°, and the resulting ester was a pale brown, viscid liquid:

$\alpha^{20}_{\mathrm{D}}\ -16{\cdot}35^\circ;\ \alpha^{100}_{\mathrm{D}}\ -16{\cdot}16^\circ.$
$d^{20}_{4}=1{\cdot}003;\ d^{100}_{4}=0{\cdot}9442;\ l=3{\cdot}02$ cm.
$[\alpha]^{20}_{\mathrm{D}}\ -54{\cdot}01^\circ;\ [\alpha]^{100}_{\mathrm{D}}\ -56{\cdot}69^\circ.$
$[\mathrm{M}]^{20}_{\mathrm{D}}\ -186{\cdot}8^\circ;\ [\mathrm{M}]^{100}_{\mathrm{D}}\ -196{\cdot}2^\circ.$

Menthyl m-iso*Amyloxybenzoate*.—Methyl *m-iso*amyloxybenzoate is an oil which distils at 185°/16 mm. The acid, after recrystallisation from alcohol, melted at 74—75°. The acid chloride was prepared in benzene solution, and consisted of a brown liquid which could not be distilled. The action with menthol began at 93°, and was completed in five hours at 120°. When decolorised with animal charcoal, the ester formed a pale brown, viscid liquid:

$\alpha^{20}_{\mathrm{D}}\ -20{\cdot}89^\circ;\ \alpha^{10}_{\mathrm{D}}\ -19{\cdot}41^\circ.$
$d^{20}_{4}=0{\cdot}9947;\ d^{100}_{4}=0{\cdot}9363;\ l=3{\cdot}02$ cm.
$[\alpha]^{20}_{\mathrm{D}}\ -69{\cdot}53^\circ;\ [\alpha]^{100}_{\mathrm{D}}\ -68{\cdot}66^\circ.$
$[\mathrm{M}]^{20}_{\mathrm{D}}\ -240{\cdot}6^\circ;\ [\mathrm{M}]^{100}_{\mathrm{D}}\ -237{\cdot}6^\circ.$

Menthyl p-iso*Amyloxybenzoate*.—Methyl *p-iso*amyloxybenzoate was obtained as a pale yellow oil, which distilled at 175—177°/13 mm. The acid crystallised in colourless needles, melting at 141—142°. The acid chloride, which was prepared by the direct action of phosphorus pentachloride on the acid, was a pale red liquid, which on distillation yielded a colourless liquid, boiling at 180—182°/12 mm. The action with menthol began at 105°, and was completed at 120°. The menthyl ester is a solid, which, after crystallisation from methyl alcohol, forms colourless needles, melting at 54—55°:

α_D^{20} $-21{\cdot}51°$; α_D^{100} $-19{\cdot}18°$.
$d_4^{20}=0{\cdot}9954$; d_4^{100} $0{\cdot}9400$; $l=3{\cdot}02$ cm.
$[\alpha]_D^{20}$ $-71{\cdot}57°$; $[\alpha]_D^{100}$ $-67{\cdot}57°$.
$[M]_D^{20}$ $-247{\cdot}6°$; $[M]_D^{100}$ $-233{\cdot}8°$.

Menthyl o-*Allyloxybenzoate*, $C_6H_4(O{\cdot}C_3H_5){\cdot}CO_2{\cdot}C_{10}H_{19}$. — The methyl allyloxy-ester distilled at 163°/20 mm. The acid crystallised from dilute alcohol in shining leaflets, melting at 60—62°. The acid chloride was prepared in benzene solution, and was obtained as a dark brown liquid which could not be distilled without decomposition. The action with menthol began at 57°. The resulting ester, which was dark red, was completely decolorised by animal charcoal. After recrystallisation from alcohol, it formed colourless, glistening leaflets, melting at 61—62°:

α_D^{100} $-16{\cdot}19°$. $d_4^{100}=0{\cdot}9689$; $l=3{\cdot}02$ cm.
$[\alpha]_D^{100}$ $-55\ 35°$; $[M]_D^{100}$ $-174{\cdot}9°$.

Menthyl p-*Allyloxybenzoate*.—The methyl allyloxy-ester distilled at 163°/15 mm. It was hydrolysed with aqueous sodium hydroxide, and yielded an acid, which crystallised in leaflets, melting at 160—162°. To prepare the acid chloride, the acid was suspended in benzene, and phosphorus pentachloride added. The acid chloride dissolved, and, after removal of benzene and phosphoryl chloride, remained as a slightly discoloured liquid, which could not be distilled. The reaction with menthol began at 85°. The menthyl ester is a colourless, viscid liquid:

α_D^{20} $-24{\cdot}71°$; α_D^{100} $-21{\cdot}93°$.
$d_4^{20}=1{\cdot}027$; $d_4^{100}=0{\cdot}9689$; $l=3{\cdot}02$ cm.
$[\alpha]_D^{20}$ $-79{\cdot}69°$; $[\alpha]_D^{100}$ $-74{\cdot}95°$.
$[M]_D^{20}$ $-251{\cdot}8°$; $[M]_D^{100}$ $-236{\cdot}9°$.

Menthyl o-*Benzyloxybenzoate*, $C_6H_4(O{\cdot}C_7H_7){\cdot}CO_2{\cdot}C_{10}H_{19}$.—Thirty-one grams of methyl salicylate were heated on the water-bath with 4·6 grams of sodium dissolved in 100 c.c. of methyl alcohol, and 25 grams of benzyl chloride for eight hours. To prevent bumping and also to improve the yield, the bulk of the methyl alcohol was first removed by distilling from the water-bath. The product was shaken with sodium hydroxide solution to remove salicylic ester, and fractionated to separate benzyl chloride. Thirty-eight grams of ester were obtained, boiling at 215—217°/15 mm. It solidified, on cooling, in large, colourless, prismatic crystals, melting at 46—47° After hydrolysis with 20 per cent. sodium hydroxide solution, the liquid was extracted with ether to remove impurities, and acidified. The acid is precipitated at first as an oil, but soon solidifies, and, after crystallisation from methyl alcohol, melts at 76—77°. It was treated in the usual way with phosphorus pentachloride, and the oxychloride removed. The product was a viscid, faintly brown liquid, which readily reacted with menthol, yielding a semi-solid, transparent substance. In spite of various attempts to remove every trace of phosphoryl chloride from the acid chloride, the menthyl ester always contained an appreciable amount of phosphorus. Another preparation was therefore made with thionyl chloride in place of phosphorus chloride, which is probably purer and has a higher rotation. In the table on p. 1735 we have given the mean of the two results.

I. (PCl_5) : α_D^{20} $-15{\cdot}55°$; α_D^{100} $-13{\cdot}90°$.
II. ($SOCl_2$) : α_D^{20} $-16{\cdot}23°$; α_D^{100} $-14{\cdot}55°$.
I. $d_4^{20}=1{\cdot}147$; $d_4^{100}=1{\cdot}089$; $l=3{\cdot}02$ cm.
II. $d_4^{20}=1{\cdot}142$; $d_4^{100}=1{\cdot}083$; $l=3{\cdot}02$ cm.
I. $[\alpha]_D^{20}$ $-44{\cdot}89°$; $[\alpha]_D^{100}$ $-42{\cdot}28°$.
II. $[\alpha]_D^{20}$ $-47{\cdot}07°$; $[\alpha]_D^{100}$ $-44{\cdot}49°$.
I. $[M]_D^{20}$ $-164{\cdot}3°$; $[M]_D^{100}$ $-154{\cdot}7°$.
II. $[M]_D^{20}$ $-172{\cdot}3°$; $[M]_D^{100}$ $-162{\cdot}8°$.

Menthyl p-*Benzyloxybenzoate.*—The methyl benzyloxy-ester was prepared like the previous compound, and melted at 99°. It was hydrolysed with 20 per cent. methyl-alcoholic potassium hydroxide solution. The potassium salt, which separated on cooling, was recrystallised from water, and gave an acid, which crystallised in colourless needles, and melted at 188—190°. The acid was dissolved in four to five times its weight of benzene, and the phosphorus chloride added. On heating on the water-bath, the acid dissolved, and, on cooling, the acid chloride crystallised in colourless needles, melting at 104—106°. It was washed with light petroleum, and heated with menthol. The action began about 100°, and was completed in two hours at 140°. The substance, which remained liquid for some time, slowly crystallised:

α_D^{20} $-22{\cdot}40°$; α_D^{100} $-19{\cdot}75°$.
$d_D^{20}=1{\cdot}064$; $d_4^{100}=1{\cdot}0015$; $l=3{\cdot}02$ cm.
$[\alpha]_D^{20}$ $-69{\cdot}68°$; $[\alpha]_D^{100}$ $-65{\cdot}29°$.
$[M]_D^{20}$ $-255{\cdot}1°$; $[M]_D^{100}$ $-238{\cdot}9°$.

Menthyl o-*Dimethylaminobenzoate*, $C_6H_4(NMe_2){\cdot}CO_2{\cdot}C_{10}H_{19}$.—The *o*-dimethylamino-acid was obtained from anthranilic acid and methyl sulphate by Willstätter and Kahn's method (*Ber.*, 1904, **37**, 408). The anthranilic acid is first converted into monomethylaminobenzoic acid (m. p. 177°), then into the methyl ester, which distils at 134—135°/14 mm., and solidifies on cooling (m. p. about 15—16°). This is converted into the dimethylamino-ester, and finally by boiling with water into the acid. The acid when recrystallised from ether melts at 72°, and not at 70° as given by the authors. The acid was heated on the water-bath with three times its weight of thionyl chloride, and the excess removed in a current of dry air under diminished pressure. The residue, which had an orange colour, was mixed with menthol and heated to 100°. On shaking, a vigorous action began with evolution of hydrogen chloride, and was completed at 120°. The product was a dark red mass, from which some of the colour was removed after keeping for several days in ethereal solution with animal charcoal. It was dissolved in light petroleum, and precipitated by dry hydrogen chloride as the hydrochloride in the form of a viscid liquid. This was separated and converted into the ester without, however, any change of colour. The product gave a correct analysis, and therefore we are disposed to regard the substance as moderately pure:

α_D^{100} $-10{\cdot}24°$. $d_4^{100}=1{\cdot}019$; $l=3{\cdot}02$ cm.
$[\alpha]_D^{100}$ $-33{\cdot}29°$; $[M]_D^{100}$ $-100{\cdot}9°$.

Menthyl p-*Dimethylaminobenzoate.*—*p*-Aminobenzoic acid was converted into the dimethylamino-acid by Willstätter and Kahn's method (*loc. cit.*), and melted at 235°. It was heated with three times its weight of thionyl chloride, and, on removal of the excess of the latter, the acid chloride solidified as an orange, crystalline mass. A portion of this was warmed with methyl alcohol, and after removal of the alcohol gave a crystalline ester, which had the correct melting point (102°). It may be assumed therefore that the acid chloride was moderately pure. It was heated with menthol to 120°, and the product purified in the usual way. The ester is precipitated as hydrochloride from its solution in light petroleum, but has the same red colour as the ortho-compound both before and after precipitation, and gave nearly the same rotation number:

	Before precipitation.	After precipitation.
α_D^{100} ……………	$-25{\cdot}56°$	$-25{\cdot}33°$

$d_4^{100}=0{\cdot}9852$; $l=3{\cdot}02$ cm.
$[\alpha]_D^{100}$ $-85{\cdot}13°$; $[M]_D^{100}$ $-257{\cdot}9°$.

Menthyl α-*Methoxynaphthoate*, $C_{10}H_6(OMe){\cdot}CO_2{\cdot}C_{10}H_{19}$. — The methyl ester was obtained by the action of methyl iodide on the silver salt of α-hydroxynaphthoic acid. It forms red, prismatic crystals, which, on recrystallisation from alcohol with the addition of charcoal, become colourless, and melt at 74—76°. The methoxy-ester is a dark red oil, which became pale yellow on distillation, and boiled at 193—195°/17 mm. It was hydrolysed with 20 per cent. sodium hydroxide solution. The addition of alkali immediately produced a red colour, and this red colour was also observed in the different alkaline salts of the original hydroxynaphthoic acid. The methoxy-acid, on recrystallisation from alcohol, gave colourless needles, melting at 120—123°. The acid chloride, which was prepared by the action of phosphorus pentachloride in benzene solution, crystallises in fine, colourless needles. The reaction with menthol began at 87°, and was completed at 120° in five and a-half hours. The ester is a very viscid, pale yellow substance:

α_D^{20} $-25{\cdot}43°$; α_D^{100} $-21{\cdot}69°$.
$d_4^{20}=1{\cdot}076$; $d_4^{100}=1{\cdot}022$; $l=3{\cdot}02$ cm.
$[\alpha]_D^{20}$ $-78{\cdot}27°$; $[\alpha]_D^{100}$ $-70{\cdot}32°$.
$[M]_D^{20}$ $-266{\cdot}2°$; $[M]_D^{100}$ $-239{\cdot}0$.

Menthyl β-Methoxynaphthoate.—β-Hydroxynaphthoic acid was converted into the methyl ester by boiling 50 grams with 200 c.c. of methyl alcohol and 10 c.c. of concentrated sulphuric acid. It yielded 46 grams of crude ester, which, after crystallisation from alcohol, consisted of pale yellow needles (m. p. 73—74°). This was converted in the usual way into the methoxy-ester, boiling at 217°/20 mm. It solidified, on cooling, in massive plates (m. p. 45—47°). It was hydrolysed in the ordinary way, and the acid, when crystallised from alcohol, melted at 126—130°. It was converted into the acid chloride by heating with an equal weight of phosphorus pentachloride, and, when freed from oxychloride, crystallised. The action with menthol began on warming gently. The menthyl ester solidified; it melts at 88·5—90°:

α_D^{20} $-16{\cdot}20°$; α_D^{100} $-14{\cdot}50°$.
$d_4^{20}=1{\cdot}083$; $d_4^{100}=1{\cdot}025$; $l=3{\cdot}02$ cm.
$[\alpha]_D^{20}$ $-48{\cdot}94°$; $[\alpha]_D^{100}$ $-46{\cdot}84°$.
$[M]_D^{20}$ $-166{\cdot}4°$; $[M]_D^{100}$ $-159{\cdot}2°$.

Menthyl β-Benzyloxynaphthoate, $C_{10}H_6(O{\cdot}C_7H_7){\cdot}CO_2{\cdot}C_{10}H_{19}$.—The methyl ester was obtained by acting on the sodium compound of β-hydroxynaphthoic ester with benzyl chloride, and formed a dark red, viscid liquid, which could not be distilled. It was hydrolysed with 20 per cent. alcoholic potash. The acid was precipitated as a sticky mass, which solidified on keeping, and crystallised from alcohol in colourless needles, melting at 130—132°. The acid chloride was obtained as a hard, transparent, yellow mass by the action of phosphorus pentachloride in benzene solution. The menthyl ester was prepared by heating the acid chloride with menthol to 120° for six and a-half hours. The reaction began at 85°. The menthyl ester is a brown, transparent solid, which is very viscid at 100°:

α_D^{20} $-29{\cdot}46°$; α_D^{100} $-24{\cdot}87°$.
$d_4^{20}=1{\cdot}118$; $d_4^{100}=1{\cdot}058$; $l=3{\cdot}02$ cm.

$[\alpha]_D^{20}$ −87·27°; $[\alpha]_D^{100}$ −77·82°.
$[M]_D^{20}$ −363·0°; $[M]_D^{100}$ −324·4°.

Menthyl o-*Toluate*, $C_6H_4Me\cdot CO_2\cdot C_{10}H_{19}$.—The acid chloride, prepared by the action of phosphorus pentachloride on the acid, is a colourless liquid (b. p. 99—103°/11 mm.). The action with menthol began at 68°. The menthyl ester is a colourless, viscid liquid, which distils at 213—215°/25 mm.:

	Undistilled.	Distilled.
α_D^{20}	−25·45°	−25·43°
α_D^{100}	23·05	23·07

$d_4^{20} = 0·9982$; $d_4^{100} = 0·9383$; $l = 3·02$ cm.
$[\alpha]_D^{20}$ −84·35°; $[\alpha]_D^{100}$ −81·41°.
$[M]_D^{20}$ −231·1°; $[M]_D^{100}$ −223·1°.

Menthyl m-*toluate* was prepared as above. The acid chloride is a colourless liquid, boiling at 136—138°/31 mm. The reaction with menthol began at 97°. The menthyl ester is a colourless, rather viscid liquid, boiling at 228—229°/36 mm.:

	Undistilled.	Distilled.
α_D^{20}	−26·47°	−26·31°
α_D^{100}	24·29	24·18

$d_4^{20} = 0·9946$; $d_4^{100} = 0·9352$; $l = 3·02$ cm.
$[\alpha]_D^{20}$ −87·59°; $[\alpha]_D^{100}$ −85·63°.
$[M]_D^{20}$ −240·0°; $[M]_D^{100}$ −234·7°.

Menthyl p-*toluate* was prepared as above. The acid chloride is a colourless liquid. The reaction with menthol began at 78°. The menthyl ester is a colourless, crystalline substance, boiling at 196—198°/11 mm., and melting at 40—41°:

	Undistilled.	Distilled.
α_D^{20}	−27·02°	−26·99°
α_D^{100}	24·36	24·40

$d_4^{20} = 0·9937$; $d_4^{100} = 0·9336$; $l = 3·02$ cm.
$[\alpha]_D^{20}$ −89·93°; $[\alpha]_D^{100}$ −86·56°.
$[M]_D^{20}$ −246·4°; $[M]_D^{100}$ −237·2°.

Menthyl Phenylacetate, $C_6H_5\cdot CH_2\cdot CO_2\cdot C_{10}H_{19}$.—The action of menthol on phenylacetyl chloride began at 50°. The ester is a colourless, mobile liquid, boiling at 192—197°/10 mm.:

	Undistilled.	Distilled.
α_D^{20}	−20·85°	−20·79°
α_D^{100}	18·74	18·61

$d_4^{20} = 1·002$; $d_4^{100} = 0·9400$; $l = 3·02$ cm.
$[\alpha]_D^{20}$ −68·70°; $[\alpha]_D^{100}$ −65·56°.
$[M]_D^{20}$ −188·2°; $[M]_D^{100}$ −179·6°.

Menthyl benzoate, $C_6H_5{\cdot}CO_2{\cdot}C_{10}H_{19}$, was obtained by the action of menthol on benzoyl chloride, which began at 88°. The ester is a colourless, crystalline solid, melting at 54°. In order to determine the rotation and density at 20°, the rotation at 100° was first determined, and the liquid allowed to cool somewhat, when a current of water at 20° was allowed to run through the jacket of the polarimeter tube for some time. As soon as the first indications of crystallisation appeared, a reading was taken, and the process repeated. The density was first taken in the pyknometer at 100°, and then the liquid supercooled in water at 20°. As crystallisation always commenced at the ends of the limbs, it was found that by keeping the ends warm by touching them occasionally with the tip of a Bunsen flame, crystallisation could be prevented for any length of time:

$\alpha_{\mathrm{D}}^{20}\ -27{\cdot}83^\circ$; $\alpha_{\mathrm{D}}^{100}\ -25{\cdot}45^\circ$.
$d_4^{20}=1{\cdot}002$; $d_4^{100}=0{\cdot}9417$; $l=3{\cdot}02$ cm.
$[\alpha]_{\mathrm{D}}^{20}\ -91{\cdot}95^\circ$; $[\alpha]_{\mathrm{D}}^{100}\ -89{\cdot}47^\circ$.
$[\mathrm{M}]_{\mathrm{D}}^{20}\ -239{\cdot}0^\circ$; $[\mathrm{M}]_{\mathrm{D}}^{100}\ -232{\cdot}7^\circ$.

The following table contains the analytical results:

Ester.	Substance taken.	CO_2.	H_2O.	C found.	C calc.	H found.	H calc.
o-Methoxybenzoic ester......	0·1409	0·3855	0·1149	74·64	74·48	9·05	8·96
m-Methoxybenzoic ,, ...	0·1364	0·3721	0·1083	74·39		8·82	
p-Methoxybenzoic ,, ...	0·1542	0·4200	0·1248	74·27		8·99	
o-Ethoxybenzoic ,, ...	0·1423	0·3874	0·1184	74·27	74·56	9·17	9·24
m-Ethoxybenzoic ,, ...	0·1432	0·3921	0·1197	74·68		9·30	
p-Ethoxybenzoic ,, ...	0·1544	0·4216	0·1295	74·47		9·32	
o-Propoxybenzoic ,, ...	0·1641	0·4539	0·1385	75·50	75·50	9·37	9·40
m-Propoxybenzoic ,, ...	0·1645	0·4558	0·1410	75·60		9·50	
p-Propoxybenzoic ,, ...	0·1551	0·4289	0·1330	75·44		9·53	
o-*iso*Propoxybenzoic ester...	0·1680	0·4560	0·1404	74·10		9·29	
p-*iso*Propoxybenzoic ,, ...	0·1674	0·4616	0·1412	75·20		9·37	
o-*iso*Amyloxybenzoic ,, ...	0·1618	0·4508	0·1431	76·0	76·30	9·83	9·80
m-*iso*Amyloxybenzoic ,, ...	0·1550	0·4280	0·1374	75·43		9·85	
p-*iso*Amyloxybenzoic ,, ...	0·1432	0·3982	0·1265	75·90		9·81	
o-Allyloxybenzoic ,, ...	0·1587	0·4410	0·1274	75·80	76·0	8·92	8·8
p-Allyloxybenzoic ,, ...	0·1589	0·4414	0·1261	75·80		8·82	
o-Benzyloxybenzoic ,, ...	0·1612	0·4620	0·1061	78·20	78·70	7·32	8·20
p-Benzyloxybenzoic ,, ...	0·1618	0·4653	0·1231	78·50		8·45	
α-Methoxynaphthoic ,, ...	0·1639	0·4655	0·1221	77·55	77·70	8·27	8·20
β-Methoxynaphthoic ,, ...	0·1357	0·3865	0·1008	77·67		8·25	
β-Benzyloxynaphthoic ester	0·1649	0·4849	0·1132	80·29	80·76	7·62	7·69

o-Dimethylaminobenzoic ester: 0·2264 gave 9·5 c.c. N_2 (moist) at 19° and 752 mm. N = 4·80. Calc., N = 4·90 per cent.

p-Dimethylaminobenzoic ester: 0·2105 gave 8·3 c.c. N_2 (moist) at 21° and 744 mm. N = 4·52. Calc., N = 4·90 per cent.

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the preparation of the three ethoxybenzoic esters. We also desire to thank the Research Fund Committee of the Chemical Society for funds which have defrayed the greater part of the cost of the materials used in the above investigation.

THE UNIVERSITY,
LEEDS.

CLXXXV.—*A Study of Some Unsaturated Compounds Containing the* tert.*-Butyryl Group. Part I.*

By ALFRED ARCHIBALD BOON and FORSYTH JAMES WILSON.

ONE of us has recently shown that the action of phosphorus pentasulphide on desylpinacoline appears to be abnormal (this vol., p. 1257). With the view of investigating the action of organic compounds of sulphur on substances containing the *tert.*-butyryl group, we intend studying some of the ketones having the general formula $R\cdot CH{:}CH\cdot CO\cdot CMe_3$, where R is invariably an aryl radicle. Some years ago a number of such compounds, which are related to benzylidenepinacoline (*Ber.*, 1897, **30**, 2268), were prepared by us. One of these, namely, furylidenepinacoline,

$$C_4H_3O\cdot CH{:}CH\cdot CO\cdot CMe_3,$$

a pale yellow, oily liquid with a very characteristic odour, was found to be vigorously attacked by bromine with apparent decomposition; so we were induced to try the action of bromine on some of our other preparations. The results of our investigation on piperonylidenepinacoline form the subject of this communication. By means of aqueous sodium hydroxide, piperonal can be condensed with pinacoline in alcoholic solution, with the formation of *piperonylidenepinacoline* (*α-*tert.*-butyryl-β-piperonylethylene*), according to the following equation:

$$CH_2{:}O_2{:}C_6H_3\cdot CHO + CH_3\cdot CO\cdot CMe_3 = CH_2{:}O_2{:}C_6H_3\cdot CH{:}CH\cdot CO\cdot CMe_3 + H_2O.$$

This compound melts at 94—95°, and is attacked by bromine at the ordinary temperature, forming chiefly piperonylidenepinacoline dibromide, $CH_2{:}O_2{:}C_6H_3\cdot CHBr\cdot CHBr\cdot CO\cdot CMe_3$ (m. p. 138—139°), and also, to a small extent, another substance, which apparently is a monobromo-compound (m. p. 110—111°), and may be represented by either of the following formulæ:

$$\underset{\alpha\text{-Compound.}}{CH_2{:}O_2{:}C_6H_3\cdot CH{:}CBr\cdot CO\cdot CMe_3} \text{ or } \underset{\beta\text{-Compound.}}{CH_2{:}O_2{:}C_6H_3\cdot CBr{:}CH\cdot CO\cdot CMe_3.}$$

In brominating piperonylidenepinacoline, we tried various solvents. Chloroform was found to be the best, glacial acetic acid suitable, but carbon disulphide of very little value, very poor yields being obtained in this case.

When piperonylidenepinacoline dibromide was boiled with absolute alcohol, after a time it was found that the latter gave an acid reaction, and a compound was ultimately obtained which still contained bromine. These facts, coupled with our analysis of the substance, appeared to show that one of the bromine atoms of piperonylidenepinacoline dibromide had been replaced by an ethoxy-group:

$$CH_2{:}O_2{:}C_6H_3{\cdot}CHBr{\cdot}CHBr{\cdot}CO{\cdot}CMe_3 \xrightarrow[-HBr]{+EtOH}$$
$$CH_2{:}O_2{:}C_6H_3{\cdot}CHBr{\cdot}CH(OEt){\cdot}CO{\cdot}CMe_3 \ (\alpha)$$
$$\text{or } CH_2{:}O_2{:}C_6H_3{\cdot}CH(OEt){\cdot}CHBr{\cdot}CO{\cdot}CMe_3 \ (\beta)$$

This compound melts at 82—83°, and was found to be identical with that produced by boiling piperonylidenepinacoline dibromide with one molecular proportion of potassium hydroxide in alcoholic solution, the above reaction no doubt taking place, but the hydrobromic acid in this case being neutralised by the alkali present. When, however, piperonylidenepinacoline dibromide was treated with two molecular proportions of potassium hydroxide in alcoholic solution, three compounds were obtained. One of these, which constituted the chief product of the reaction, was *ethoxypiperonylidenepinacoline*, which we have provisionally formulated as the β-compound, $CH_2{:}O_2{:}C_6H_3{\cdot}C(OEt){:}CH{\cdot}CO{\cdot}CMe_3$ (m. p. 112—113°).

The other compounds were: a substance having the same composition as the β-compound and probably isomeric with it (α-compound) (m. p. 86—87°), and also a substance containing bromine, which appeared to be identical with the ethoxy-derivative (α or β) (m. p. 82—83°) already referred to.

The latter substance seems therefore to be the initial product of the reaction, and hence the possible changes involved in the formation of the compounds, obtained when an alcoholic solution of potassium hydroxide is allowed to act on piperonylidenepinacoline dibromide, may be represented by the following scheme:

I. $R{\cdot}CHBr{\cdot}CHBrR' + EtOH = R{\cdot}CHBr{\cdot}CH(OEt)R'(\alpha) + HBr$
(neutralised by KOH)

or $R{\cdot}CH(OEt){\cdot}CHBrR'(\beta) + HBr$
(neutralised by KOH)

II. $R{\cdot}CHBr{\cdot}CH(OEt)R' + KOH = R{\cdot}CH{:}C(OEt)R'(\alpha) + KBr + H_2O.$
(M. p. 86—87°).

and $R{\cdot}CH(OEt){\cdot}CHBrR' + KOH = R{\cdot}C(OEt){:}CHR'(\beta) +$
(M.p. 112—113°) $KBr + H_2O.$

where R and R′ represent respectively $CH_2{:}O_2{:}C_6H_3{\cdot}$ and ${\cdot}CO{\cdot}CMe_3$.

These ethoxy-compounds may, however, be stereoisomerides, and it is interesting to note that they are analogues of the ethyl ether of dibenzoylmethane obtained by Ruhemann and Watson in their critical study of Wislicenus's isomeride of dibenzoylmethane (Trans., 1904, **85**, 456). Piperonylidenepinacoline, when acted on by hydroxylamine hydrochloride at the ordinary temperature, yields an *oxime* (m. p. 144—145°).

EXPERIMENTAL.

Piperonylidenepinacoline (α-tert.-*Butyryl-β-piperonylethylene*), $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CO{\cdot}CMe_3$.

To a solution containing 90 grams of piperonal and 64 grams of pinacoline in 450 c.c. of absolute alcohol, 100 c.c. of a 10 per cent. solution of sodium hydroxide were added. This mixture was heated for ten minutes on a water-bath, and then kept for twenty-four hours at the ordinary temperature.

The crystalline mass thus obtained was collected, and to the filtrate 50 c.c. of a 20 per cent. solution of sodium hydroxide were added. After keeping for a day, a crystalline precipitate was again obtained; this was collected, and the filtrate, to which 25 c.c. of a 20 per cent. solution of sodium hydroxide were added, was kept for two days. A further yield of the crude crystalline product was thus collected, and the filtrate precipitated with water. The various crops of the crude mother substance obtained in these operations were purified by crystallisation from boiling alcohol. The yield was extremely good:

0·1824 gave 0·4823 CO_2 and 0·1141 H_2O. C = 72·11; H = 6·95.
0·1891 „ 0·5007 CO_2 „ 0·1179 H_2O. C = 72·21; H = 6·93.
0·1993, in 48·15 of nitrobenzene, gave $\Delta t = -0·127°$. M.W. = 228.
$C_{14}H_{16}O_3$ requires C = 72·41; H = 6·89 per cent. M.W. = 232.

Piperonylidenepinacoline melts at 94—95°. When crystallised from absolute alcohol, it is obtained in pale yellow needles. It is very soluble in benzene or chloroform, but less so in light petroleum.

Action of Bromine on Piperonylidenepinacoline.

As stated in the introduction, chloroform was found to be the best solvent in this reaction. Piperonylidenepinacoline was dissolved in dry chloroform, the calculated quantity of dry bromine (2 mols.), dissolved in dry chloroform, was gradually added, and the solvent afterwards removed by a current of dry air. The residue was then fractionally crystallised from glacial acetic acid. A very good yield (75 per cent.) of *piperonylidenepinacoline dibromide*,

$CH_2{:}O_2{:}C_6H_3{\cdot}CHBr{\cdot}CHBr{\cdot}CO{\cdot}CMe_3$, which was the main product, was thus obtained:

0·2548 gave 0·2458 AgBr. Br = 41·02.
0·1171 „ 0·1124 AgBr. Br = 40·93.
$C_{14}H_{16}O_3Br_2$ requires Br = 40·81 per cent.

Piperonylidenepinacoline dibromide melts at 138—139°, and can be obtained in colourless needles from light petroleum, in which it is sparingly soluble. It dissolves readily in benzene, but less so in acetic acid. In this reaction, to a small extent, another substance was obtained in short, colourless prisms from light petroleum. It was found to be more soluble in acetic acid (and the other solvents mentioned above) than the dibromide, and appears to be a *monobromide* of *piperonylidenepinacoline*:

$CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CBr{\cdot}CO{\cdot}CMe_3$, α-compound, or
$CH_2{:}O_2{:}C_6H_3{\cdot}CBr{:}CH{\cdot}CO{\cdot}CMe_3$, β-compound.

This substance melts at 110—111°, and is apparently unsaturated, as it combines with bromine in chloroform solution:

0·1659 was found equivalent to 5·15 c.c. $N/10$-$AgNO_3$. Br = 24·83.
$C_{14}H_{15}O_3Br$ requires Br = 25·72 per cent.

A number of analyses were made of this compound, but in every case the result obtained was low.

Action of Ethyl Alcohol on Piperonylidenepinacoline Dibromide: Formation of Bromoethoxypiperonylidenepinacoline.

$CH_2{:}O_2{:}C_6H_3{\cdot}CHBr{\cdot}CH(OEt){\cdot}CO{\cdot}CMe_3$, α-compound, or
$CH_2{:}O_2{:}C_6H_3{\cdot}CH(OEt){\cdot}CHBr{\cdot}CO{\cdot}CMe_3$, β-compound.

Piperonylidenepinacoline dibromide was boiled with absolute alcohol, in which it gradually dissolved, the solution giving an acid reaction. After about four hours' boiling, the solution, on cooling, deposited fine, colourless needles, which were collected and recrystallised from boiling alcohol. As mentioned above, in this reaction an atom of bromine in the dibromide is apparently replaced by an ethoxy-group:

0·1474 was found equivalent to 4·10 c.c. $N/10$-$AgNO_3$. Br = 22·25.
$C_{16}H_{21}O_4Br$ requires Br = 22·40 per cent.

Bromoethoxypiperonylidenepinacoline melts at 82—83°, and can also be obtained by the action of one molecule of potassium hydroxide on an alcoholic solution of piperonylidenepinacoline dibromide. An estimation of the bromine contained in the compound obtained by this method gave the following result:

0·1850 was found equivalent to 5·20 c.c. $N/10$-$AgNO_3$. Br = 22·49.
$C_{16}H_{21}O_4Br$ requires Br = 22·40 per cent.

(The average result of a number of analyses, made with samples obtained by both methods of production, gave Br = 22·12 per cent.)

Action of Potassium Hydroxide (2 mols.) *on Piperonylidenepinacoline Dibromide in Alcoholic Solution: Formation of Ethoxypiperonylidenepinacoline* (*α and β*).

$CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}C(OEt){\cdot}CO{\cdot}CMe_3$, α-compound (?), and
$CH_2{:}O_2{:}C_6H_3{\cdot}C(OEt){:}CH{\cdot}CO{\cdot}CMe_3$, β-compound (?).

Piperonylidenepinacoline dibromide was dissolved in hot alcohol, and the necessary quantity (2 mols.) of potassium hydroxide dissolved in absolute alcohol added; potassium bromide was at once precipitated, and, to complete the action, the mixture was warmed for one hour on the water-bath. The solution, after being filtered, was evaporated, and the residue extracted with ether to remove potassium bromide. The ethereal solution was next evaporated, and the residue recrystallised from light petroleum. In this way there was obtained a colourless, crystalline substance, which, after recrystallisation from alcohol, and then from a mixture of benzene and light petroleum, melted at 112—113°. This constituted the main product of the reaction. From the mother liquor there was obtained—in small amount only—a colourless, crystalline substance, which, after recrystallisation from alcohol, melted at 86—87°. The light petroleum mother liquors, on evaporation, gave a large quantity of oil, which, after some time, partly solidified, giving a further yield of the main product (m. p. 112—113°), whilst the residual oil, on cooling and long keeping, solidified to some extent, and yielded a substance melting at 82—83°, which in its general behaviour was apparently identical with the substance, $CH_2{:}O_2{:}C_6H_3{\cdot}CHBr{\cdot}CH(OEt){\cdot}CO{\cdot}CMe_3$ or $CH_2{:}O_2{:}C_6H_3{\cdot}CH(OEt){\cdot}CHBr{\cdot}CO{\cdot}CMe_3$, already mentioned.

The analytical results for the substances melting at 112—113° and 86—87° are as follows:

Substance melting at 112—113°.

0·1122 gave 0·2857 CO_2 and 0·0750 H_2O. C = 69·43; H = 7·48.
0·1195 „ 0·3044 CO_2 „ 0·0782 H_2O. C = 69·46; H = 7·28.
0·3010, in 25·33 of nitrobenzene, gave $\Delta t = -0·290°$. M.W. = 285.
$C_{16}H_{20}O_4$ requires C = 69·56; H = 7·24 per cent. M.W. = 276.

Substance melting at 86—87°.

0·1382 gave 0·3552 CO_2 and 0·0907 H_2O. C = 70·09; H = 7·29.
$C_{16}H_{20}O_4$ requires C = 69·56; H = 7·24 per cent.

Action of Hydroxylamine on Piperonylidenepinacoline.

Piperonylidenepinacoline yields an *oxime*, $C_{14}H_{17}O_3N$. This was prepared by the action of 2·08 grams of hydroxylamine hydrochloride on 2·32 grams of the ketone in presence of 3 grams of potassium acetate. The oxime was precipitated by the addition of water, and purified by recrystallisation from alcohol. It is a colourless, crystalline substance, melting at 144—145°:

0·1880 gave 9·8 c.c. N_2 (moist) at 16·6° and 741 mm. N = 5·92.
0·1630 „ 8·5 c.c. N_2 (moist) „ 21·6° „ 767 mm. N = 5·94.
$C_{14}H_{17}O_3N$ requires N = 5·67 per cent.

We are continuing this investigation, more particularly with the object of obtaining some knowledge of the constitution of the ethoxy-derivatives mentioned above, and of extending our work to substances having the general formula $R\cdot CH\colon CH\cdot CO\cdot CMe_3$ referred to in the introduction.

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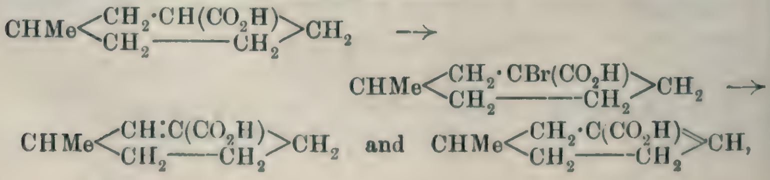
CLXXVI.—*Carboxylic Acids of* cyclo*Hexanone and some of its Derivatives.*

By HENRY DENT GARDNER, WILLIAM HENRY PERKIN, jun., and HUBERT WATSON.

THE present investigation had for its principal object an attempt to devise a method by which certain unsaturated acids, required for synthetical experiments in the terpene group, could be obtained in quantity sufficient for that purpose. It has, for example, already been shown (Perkin and Tattersall, Trans., 1905, **87**, 1085) that *m*-toluic acid is converted by reduction and subsequent bromination and elimination of hydrogen bromide into a mixture of 1-methyl-Δ^1- and Δ^3-*cyclo*hexene-3-carboxylic acids:



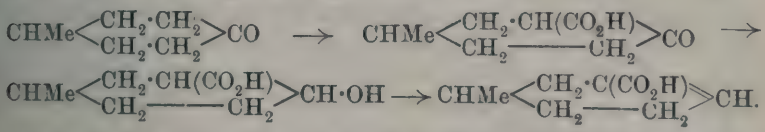
$$CHMe<\begin{matrix}CH_2\cdot CH(CO_2H)\\CH_2\text{———}CH_2\end{matrix}>CH_2 \longrightarrow CHMe<\begin{matrix}CH_2\cdot CBr(CO_2H)\\CH_2\text{———}CH_2\end{matrix}>CH_2 \longrightarrow$$

$$CHMe<\begin{matrix}CH\colon C(CO_2H)\\CH_2\text{———}CH_2\end{matrix}>CH_2 \text{ and } CHMe<\begin{matrix}CH_2\cdot C(CO_2H)\\CH_2\text{———}CH_2\end{matrix}>CH,$$

but the process, involving, as it does, reduction with sodium and *iso*amyl alcohol, is an unpleasant and tedious one, and, furthermore, the isomeric acids are difficult to separate. Consequently, the terpineols and terpenes obtained from these acids could not be investigated in so thorough a manner as was desirable.

Now, it seemed possible that a more convenient method of preparation of 1-methyl-Δ^3-*cyclo*hexene-3-carboxylic acid might result from the following series of decompositions.

1-Methyl*cyclo*hexan-4-one, which is now readily obtained in quantity from *p*-cresol by the Sabatier-Senderens process, might be readily converted into 1-methyl*cyclo*hexan-4-one-3-carboxylic acid by the action of sodamide and carbon dioxide, and this acid, on reduction, should yield 1-methyl*cyclo*hexan-4-ol-3-carboxylic acid, from which by the elimination of water, 1-methyl-Δ^3-*cyclo*hexene-3-carboxylic acid might be expected to result:

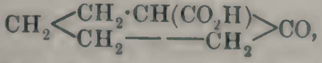


$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{CO} \longrightarrow \mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH(CO_2H)}\\ \mathrm{CH_2 —— CH_2}\end{matrix}{>}\mathrm{CO} \longrightarrow$$

$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH(CO_2H)}\\ \mathrm{CH_2 —— CH_2}\end{matrix}{>}\mathrm{CH\cdot OH} \longrightarrow \mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot C(CO_2H)}\\ \mathrm{CH_2 —— CH_2}\end{matrix}{\geqslant}\mathrm{CH}.$$

In a later communication it will be shown that this unsaturated acid may, in fact, be conveniently prepared by this process, and in quantity sufficient to allow of the complete characterisation of the terpineol and terpene derived from it. It has also been found possible to prepare sufficient of this acid to allow of its resolution by means of the brucine salt, and the preparation and examination of the active terpineols and terpenes derived from the *d*- and *l*-acids thus obtained is in active progress. There can be no doubt that other unsaturated acids of this kind will result from a similar series of reactions carried out with the aid of suitable derivatives of *cyclo*hexanone. The action of sodium or sodamide and carbon dioxide on cyclic ketones does not appear to have been investigated, and the present communication deals with the conditions under which such action takes place, and with the reduction of the resulting ketonic acids to the corresponding hydroxy-acids.

Because it is the cyclic ketone that is most readily obtained in a pure condition, the first experiments were made with *cyclo*hexanone itself, and it was found that this ketone is converted into *cyclo*hexanone-2-carboxylic acid:

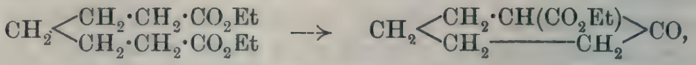


$$\mathrm{CH_2}{<}\begin{matrix}\mathrm{CH_2\cdot CH(CO_2H)}\\ \mathrm{CH_2 —— CH_2}\end{matrix}{>}\mathrm{CO},$$

when its solution in ether is treated first with sodamide and then with carbon dioxide.

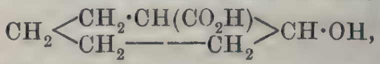
The ester of this acid had already been prepared by Dieckmann

(*Annalen*, 1901, **317**, 93) from ethyl pimelate by the action of sodium:



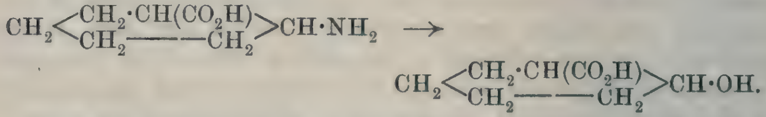
$$\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2\cdot CH_2\cdot CO_2Et}\\ \mathrm{CH_2\cdot CH_2\cdot CO_2Et}\end{matrix} \longrightarrow \mathrm{CH_2}<\begin{matrix}\mathrm{CH_2\cdot CH(CO_2Et)}\\ \mathrm{CH_2}\text{———}\mathrm{CH_2}\end{matrix}>\mathrm{CO},$$

but, owing to its instability, it was not found possible to obtain the free acid by the hydrolysis of this ester. *cyclo*Hexanone-2-carboxylic acid melts and decomposes at 81—82°, and gives an intense purple coloration when ferric chloride is added to its aqueous solution. It is readily reduced by sodium amalgam to *cyclo*hexanol-2-carboxylic acid (hexahydrosalicylic acid):



$$\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2\cdot CH(CO_2H)}\\ \mathrm{CH_2}\text{———}\mathrm{CH_2}\end{matrix}>\mathrm{CH\cdot OH},$$

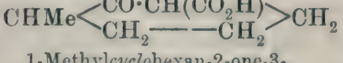
which melts at 111°, and had already been obtained by Dieckmann (*Ber.*, 1894, **27**, 2745) from ethyl *cyclo*hexanone-2-carboxylate by reduction with sodium amalgam and water. It is well known that, when salicylic acid is reduced in *iso*amyl-alcoholic solution with sodium, it does not yield hexahydrosalicylic acid, but that fission of the ring occurs, and the product is pimelic acid. Einhorn and Meyenberg (*Ber.*, 1894, **27**, 2466), however, showed that anthranilic acid may be reduced to hexahydroanthranilic acid, and that this acid, when treated with nitrous acid, is decomposed with formation of hexahydrosalicylic acid:



$$\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2\cdot CH(CO_2H)}\\ \mathrm{CH_2}\text{———}\mathrm{CH_2}\end{matrix}>\mathrm{CH\cdot NH_2} \longrightarrow \mathrm{CH_2}<\begin{matrix}\mathrm{CH_2\cdot CH(CO_2H)}\\ \mathrm{CH_2}\text{———}\mathrm{CH_2}\end{matrix}>\mathrm{CH\cdot OH}.$$

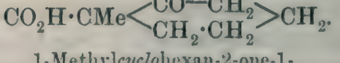
We next experimented on the action of sodamide and carbon dioxide on 1-methyl*cyclo*hexan-2-one, and obtained 1-*methyl*cyclo*hexan*-2-*one*-3-*carboxylic acid*, and from this, by reduction with sodium amalgam, we prepared 1-*methyl*cyclo*hexan*-2-*ol*-3-*carboxylic acid*.

With regard to the constitution of the keto-acid, it is clear that there are two isomerides which might conceivably be produced by the action of sodamide and carbon dioxide on 1-methyl*cyclo*hexan-2-one, namely:



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CO\cdot CH(CO_2H)}\\ \mathrm{CH_2}\text{———}\mathrm{CH_2}\end{matrix}>\mathrm{CH_2}$$

and

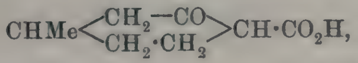


$$\mathrm{CO_2H\cdot CMe}<\begin{matrix}\mathrm{CO}\text{—}\mathrm{CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH_2}.$$

1-Methyl*cyclo*hexan-2-one-3-carboxylic acid.

1-Methyl*cyclo*hexan-2-one-1-carboxylic acid.

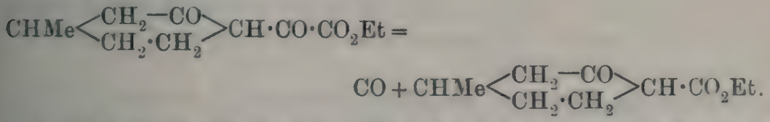
Since, however, the acid actually produced gives an intense coloration with ferric chloride, it cannot be 1-methyl*cyclo*hexan-2-one-1-carboxylic acid, and must therefore be 1-methyl*cyclo*hexan-2-one-3-carboxylic acid. More interesting results were obtained during the course of our experiments on the action of sodamide and carbon dioxide on 1-methyl*cyclo*hexan-3-one. We investigated, in the first place, the behaviour of the *dl*-ketone under these conditions, and found that it was comparatively readily converted into a keto-acid, which is probably dl-1-*methyl*cyclo*hexan-3-one-4-carboxylic acid*:



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2{-}CO}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}{>}\mathrm{CH{\cdot}CO_2H},$$

but in which the carboxyl group may possibly occupy the 2-position.

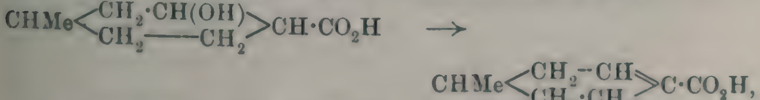
This acid melts at 100—103°, yields an ester distilling at 132—135°/24 mm., and is reduced by sodium amalgam to dl-1-*methyl*cyclo*hexan-3-ol-4-carboxylic acid* (m. p. 129—130°). Ethyl 1-methyl*cyclo*hexan-3-one-4-carboxylate had already been prepared by Kötz and Hesse (*Annalen*, 1905, **342**, 310) from 1-methyl*cyclo*hexan-3-one by condensation with ethyl oxalate and subsequent distillation of the ethyl 1-methyl*cyclo*hexan-3-one-4-oxalate thus produced:



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2{-}CO}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}{>}\mathrm{CH{\cdot}CO{\cdot}CO_2Et} = \mathrm{CO} + \mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2{-}CO}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}{>}\mathrm{CH{\cdot}CO_2Et}.$$

These investigators give 115°/12 mm. as the boiling point of this ester, and they were unable to obtain the free acid by hydrolysing it, because of the readiness with which it is decomposed into methyl*cyclo*hexanone and carbon dioxide.

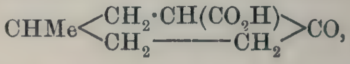
We next investigated the action of sodamide and carbon dioxide on *d*-1-methyl*cyclo*hexan-3-one from pulegone (Wallach, *Annalen*, 1896, **289**, 339), and found that, under the conditions described in the experimental part of this paper, this ketone, of specific rotation $[\alpha]_D + 8{\cdot}8°$, is converted into d-1-*methyl*cyclo*hexan-3-one-4-carboxylic acid*, which melts at 102—103°, and has $[\alpha]_D + 97{\cdot}2°$, and the ethyl ester of which has $[\alpha]_D + 84{\cdot}16°$. When the *d*-keto-acid was reduced with sodium amalgam, it yielded a d-1-*methyl*cyclo*hexan-3-ol-4-carboxylic acid*, which melted at 129—130° and had $[\alpha]_D - 31{\cdot}8°$, the sign of rotation having changed during reduction. Probably direct or indirect elimination of water will convert this acid into *d*-1-methyl-Δ^3-*cyclo*hexene-4-carboxylic acid:



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2{\cdot}CH(OH)}\\ \mathrm{CH_2{-}{-}{-}CH_2}\end{matrix}{>}\mathrm{CH{\cdot}CO_2H} \longrightarrow \mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}{\geqslant}\mathrm{C{\cdot}CO_2H},$$

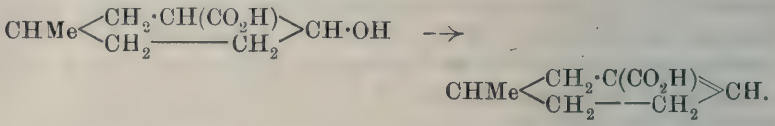
and this probability is being tested by experiment.

The investigation of the behaviour of 1-methyl*cyclo*hexan-4-one with sodamide and carbon dioxide seems to show that this ketone reacts much more readily with this reagent than is the case with the cyclic ketones which have already been mentioned. Under conditions which have been carefully worked out (p. 1769), a yield of at least 40 per cent. of 1-*methyl*cyclo*hexan*-2-*one*-3-*carboxylic acid*:



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH(CO_2H)}\\ \mathrm{CH_2\text{———}CH_2}\end{matrix}{>}\mathrm{CO},$$

is quite easily obtained. This acid melts at 101°, and is converted, by reduction, into 1-*methyl*cyclo*hexan*-4-*ol*-3-*carboxylic acid*, which melts at 114°, and, on distillation under diminished pressure, is decomposed with elimination of water and formation of 1-*methyl*-Δ^3-cyclo*hexene*-4-*carboxylic acid*:

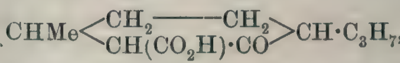


$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH(CO_2H)}\\ \mathrm{CH_2\text{———}CH_2}\end{matrix}{>}\mathrm{CH\cdot OH} \longrightarrow \mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot C(CO_2H)}\\ \mathrm{CH_2\text{——}CH_2}\end{matrix}{>}\mathrm{CH}.$$

The description of the results which have been obtained during a long investigation of this acid and its derivatives is reserved for a future communication.

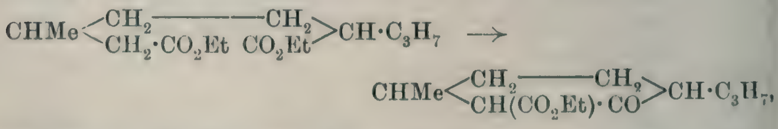
During the course of the experiments, which have been briefly summarised in the preceding pages, it appeared to us that it would be interesting to include *l*-menthone in the scope of this investigation, and the first results which we obtained seemed so puzzling that we extended our experiments also to *d*-*iso*menthone.

When *l*-menthone is treated with sodamide and carbon dioxide, under the conditions described on p. 1770, it yields a syrupy monocarboxylic acid, which doubtless has the constitution:



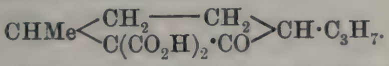
$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\text{———}CH_2}\\ \mathrm{CH(CO_2H)\cdot CO}\end{matrix}{>}\mathrm{CH\cdot C_3H_7},$$

since it gives a purple coloration when ferric chloride is added to its alcoholic solution. The ester of this acid distilled at 143—146°/12 mm., and is evidently structurally identical with the ester which Kötz and Schwarz (*Annalen*, 1907, **357**, 210) obtained from ethyl β-methyl-ε-*iso*propylpimelate by the action of sodium:



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\text{————}CH_2}\\ \mathrm{CH_2\cdot CO_2Et\ \ CO_2Et}\end{matrix}{>}\mathrm{CH\cdot C_3H_7} \longrightarrow \mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\text{———}CH_2}\\ \mathrm{CH(CO_2Et)\cdot CO}\end{matrix}{>}\mathrm{CH\cdot C_3H_7},$$

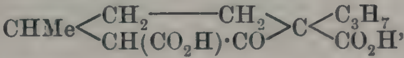
and which distilled at 145—149°/14 mm. and gave a violet coloration with ferric chloride. As well as the above menthonemonocarboxylic acid, a dicarboxylic acid is produced during the action of sodamide and carbon dioxide on *l*-menthone, and this melts at about 121—128°, and is probably a mixture of the *cis-* and *trans*-modifications of the formula



$$\mathrm{CHMe}\!<\!\begin{matrix}\mathrm{CH_2}\text{———}\mathrm{CH_2}\\ \mathrm{C(CO_2H)_2{\cdot}CO}\end{matrix}\!>\!\mathrm{CH{\cdot}C_3H_7}.$$

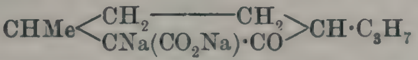
During repeated recrystallisation from ether, much decomposition took place, but we were ultimately successful in obtaining a small quantity of a dibasic acid from the mixture, which melted at 144°, and appears to be one of the above modifications in a pure state.

This acid cannot have the constitution:



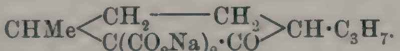
$$\mathrm{CHMe}\!<\!\begin{matrix}\mathrm{CH_2}\text{———}\mathrm{CH_2}\\ \mathrm{CH(CO_2H){\cdot}CO}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{C_3H_7}\\ \mathrm{CO_2H}\end{matrix},$$

because its solution in alcohol does not give a coloration with ferric chloride; its formation may be explained in the following manner. The sodium derivative of *iso*menthone is partly converted, by the action of carbon dioxide, into the sodium salt of *iso*menthonecarboxylic acid, which then reacts with some of the unchanged sodium *iso*menthone to yield the disodium derivative:



$$\mathrm{CHMe}\!<\!\begin{matrix}\mathrm{CH_2}\text{———}\mathrm{CH_2}\\ \mathrm{CNa(CO_2Na){\cdot}CO}\end{matrix}\!>\!\mathrm{CH{\cdot}C_3H_7}$$

(or its enolic modification), and this is then converted, by the subsequent action of the carbon dioxide, into the disodium salt of *iso*menthonedicarboxylic acid:



$$\mathrm{CHMe}\!<\!\begin{matrix}\mathrm{CH_2}\text{———}\mathrm{CH_2}\\ \mathrm{C(CO_2Na)_2{\cdot}CO}\end{matrix}\!>\!\mathrm{CH{\cdot}C_3H_7}.$$

Menthonecarboxylic acids, possessing similar properties to the above, have already been described. In 1891 (*Ber.*, **24**, 3396) Brühl, Biltz, and Cantzler treated ordinary *l*-menthone with sodium wire and carbon dioxide, and obtained a semi-solid mass, which was clearly a mixture of menthone-mono- and -di-carboxylic acids. By treatment with light petroleum, the oily monobasic acid was removed, and was not further investigated, and the insoluble, crystalline residue, after crystallisation from ether, melted at 128·5°, and was shown by analysis to be a menthonedicarboxylic acid. Oddo (*Gazzetta*, 1897, **27**, ii, 97) subsequently investigated the action of sodium and carbon dioxide on *l*-menthone, and obtained a syrupy menthonemonocarboxylic acid and a dicarboxylic acid, which melted at 140—141°.

These investigators do not appear to have determined the rotation of their acids, and, when we proceeded to investigate the acids we had prepared, we found that the monobasic as well as the dibasic acids obtained from *l*-menthone were both strongly dextrorotatory.

This result led us to prepare a quantity of *d-iso*menthone from *l*-menthone by the action of sulphuric acid (Beckmann, *Annalen*, 1888, **250**, 334), and on treating this with sodamide and carbon dioxide under exactly the same conditions as before, we found that both the mono- and di-basic acids were again strongly dextrorotatory.

A large number of experiments were then made with different samples of *l*-menthone and *d-iso*menthone, and the results, which are summarised in the following tables, show that whatever the rotation of the original *l*-menthone or *d-iso*menthone may be, the resulting mono- and di-basic acids are always dextrorotatory, and yield dextrorotatory *iso*menthones on distillation.

TABLE I.—iso*Menthonemonocarboxylic Acid.*

Rotation of original menthone, $[\alpha]_D$.	Rotation of the monocarboxylic acid, $[\alpha]_D$.	Rotation of the *iso*menthone regenerated from the acid, $[\alpha]_D$.
−24·6°	+22·6°	+19·0°
−19·1	+20·8	+17·9
−7·3	+19·4	+17·1
+8·3	+18·4	+16·9
+23·6	+22·5	+18·2
−20·3	+28·7	+15·4
−19·1	+28·3	+15·8

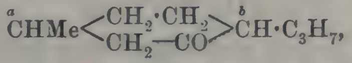
The last two experiments were made under special conditions mentioned on p. 1771.

TABLE II.—iso*Menthonedicarboxylic Acid.*

Rotation of original menthone. $[\alpha]_D$.	M. p. of dibasic acid.	Rotation of the dibasic acid. $[\alpha]_D$.	Rotation of the *iso*menthone regenerated from the acid. $[\alpha]_D$.
−24·6°	127—128°	+116·5°	—
+23·6	124—125	+107·2	—
−19·1	122—123	+102·4	—
−19·1	115	+100·3	—
−19·1	135	+121·4	+30·2°
−19·1	144	+124·4	+33·3

We next observed that, when *l*-menthone is converted into its sodium derivative by the action of sodamide on its ethereal solution, *d-iso*menthone is obtained on treatment with acids, and also that the latter by similar treatment merely suffers a slight change in rotation. Thus, in two experiments, *l*-menthone with $[\alpha]_D$ −20·3°, after treatment with sodamide, had $[\alpha]_D$ +12·0° and +15·8°, and *d-iso*menthone with $[\alpha]_D$ +14·2°, after treatment with sodamide, had $[\alpha]_D$ +15·8°. It had previously been observed that *l*-menthone is converted at least partly into *d-iso*menthone when it is treated with concentrated acids or boiled with alcoholic potassium or sodium hydroxide, and these facts and the behaviour summarised in tables I and II may be possibly explained in the following way.

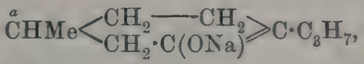
Menthone:



$$\overset{a}{\mathrm{C}}\mathrm{HMe}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2{-}CO}\end{matrix}>\overset{b}{\mathrm{C}}\mathrm{H\cdot C_3H_7},$$

contains two asymmetric carbon atoms, *a* and *b*, and the isomerism of menthone and *iso*menthone is due to differences in the nature of these.

For the sake of argument the asymmetric carbon atoms in *l*-menthone may be represented by the signs − −, and it is clear that when *l*-menthone is converted into its sodium derivative:



$$\overset{a}{\mathrm{C}}\mathrm{HMe}<\begin{matrix}\mathrm{CH_2{-\!-}CH_2}\\ \mathrm{CH_2\cdot C(ONa)}\end{matrix}\geqslant\mathrm{C\cdot C_3H_7},$$

or is treated with any agent which brings about enolic change, the asymmetry of the carbon atom *b* disappears, and the activity of the sodium derivative is due entirely to the carbon atom *a*.

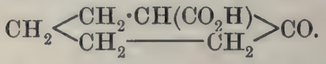
When the sodium derivative is decomposed by acids, the carbon atom *b* again becomes asymmetric, and it is probable that the presence of the active asymmetric carbon atom *a* causes the atom *b* to be produced, to some extent at least, in active form; in other words, an asymmetric synthesis is accomplished. The *d-iso*menthone which is always produced under these conditions is therefore probably a mixture of *a, b* = − − and − +, the latter predominating.

This explanation accounts, in a simple manner, for the very varying rotations which have been so often observed as the result of preparing different samples of menthone and *iso*menthone by slightly different methods. Apparently the highest rotations which have been recorded for these substances are *l*-menthone, $[\alpha]_D$ −28·46°, and *d-iso*menthone, $[\alpha]_D$ +35·1° (Beckmann, *J. pr. Chem.*, 1897, [ii], **55**, 24, 28).

It will be seen from table II that the purest specimen of *d-iso*menthonedicarboxylic acid, which we were able to obtain, melted at 144°, and on distillation yielded a *d-iso*menthone with $[\alpha]_D$ +33·3°, and which was therefore probably almost pure. On the other hand, it seems doubtful whether *l*-menthone has ever been prepared quite free from *d-iso*menthone.

EXPERIMENTAL.

cyclo*Hexanone-2-carboxylic Acid,*



$$CH_2<\begin{matrix}CH_2\cdot CH(CO_2H)\\ CH_2\text{———}CH_2\end{matrix}>CO.$$

Although this acid is so unstable, we have succeeded in isolating it in some quantity, and have analysed it and determined some of its properties. The details of the preparation are as follows. *cyclo*Hexanone * (5 grams) is dissolved in pure dry ether, finely powdered sodamide (2 grams) added, and the mixture warmed until the sodium derivative has completely separated. A current of carbon dioxide, which has been thoroughly washed and very carefully dried, is then passed slowly through the mixture for two to three hours at a temperature of 35°, the whole being well shaken from time to time and great care taken to exclude every trace of moisture. When the reaction is complete, the flask is cooled, and the product decomposed with ice and dilute hydrochloric acid and repeatedly extracted with ether. The ethereal layer is then shaken with a concentrated solution of sodium carbonate, the alkaline solution quickly cooled with powdered ice, acidified with dilute hydrochloric acid, and the *cyclo*hexanone-2-carboxylic acid, which separates as an oil, is extracted with ether.

The ethereal solution is dried, the ether partly evaporated on steam-bath under diminished pressure, and the remainder allowed to evaporate in the air, when crystals of the acid are gradually deposited.

These are left in contact with porous porcelain until quite dry, and then recrystallised from ether:

0·1438 gave 0·3105 CO_2 and 0·0919 H_2O. C=58·9; H=7·1.

$C_7H_{10}O_3$ requires C=59·1; H=7·0 per cent.

On titration with *N*/10-sodium hydroxide, 0·1314 neutralised 0·0504NaOH, whereas this amount of a monobasic acid, $C_7H_{10}O_3$, should neutralise 0·0512NaOH.

cyclo*Hexanone-2-carboxylic acid* softens at 79°, and decomposes at 81—82° into *cyclo*hexanone and carbon dioxide. It is readily soluble in water, and the aqueous solution gives a deep violet coloration on the addition of ferric chloride. It dissolves readily in ether, alcohol, benzene, or light petroleum, and separates from ether in glistening needles.

Reduction to cyclo*Hexanol-2-carboxylic acid* (hexahydrosalicylic acid).—Preliminary experiments showed that in many cases the carboxylic acids of *cyclo*hexanone and its derivatives are either not reduced at all by sodium amalgam under ordinary conditions, or, if reduced, that the process is extremely slow and often incomplete. The following modification yields, however, in most cases, excellent results.

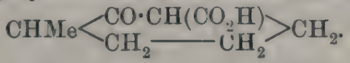
---

* The *cyclo*hexanone employed in these experiments was obtained from Poulenc Frères, and carefully purified by conversion into the sodium hydrogen sulphite derivative; it distilled at 155—156°/755 mm. and crystallised readily.

*cyclo*Hexanone-2-carboxylic acid (5 grams) is dissolved in a dilute solution of sodium carbonate, freshly prepared 3 per cent. sodium amalgam (300 grams) is slowly added, and the solution kept nearly neutral by passing a slow current of sulphur dioxide.

The product is acidified and extracted once or twice with ether in order to remove traces of unreduced keto-acid, the liquid is then saturated with ammonium sulphate, and extracted several times on the machine. The extract is dried and evaporated, and the solid mass of *cyclo*hexanol-2-carboxylic acid left in contact with porous porcelain, and then crystallised from ether, from which the acid separates in glistening prisms melting at 111°. (Found, C = 58·0; H = 8·2. Calc., C = 58·3; H = 8·3 per cent.)

1-*Methyl*cyclo*hexan-2-one-3-carboxylic Acid*,



$$\mathrm{CHMe}\left<\begin{matrix}\mathrm{CO\cdot CH(CO_2H)}\\ \mathrm{CH_2\text{———}CH_2}\end{matrix}\right>\mathrm{CH_2}.$$

The 1-methyl*cyclo*hexan-2-one used in these experiments was prepared by ourselves from *o*-cresol by the Sabatier-Senderens process, and then very carefully separated from 1-methyl*cyclo*hexan-2-ol and other impurities by conversion into the sodium hydrogen sulphite derivative. It distilled at 164—165° (compare Wallach, *Annalen*, 1906, **346**, 251). The conversion into the sodium derivative by means of sodamide and the subsequent treatment with carbon dioxide was carried out at the ordinary temperature in the manner described on p. 1764, carefully purified light petroleum being used as the solvent in the place of ether. The product was mixed with powdered ice and dilute hydrochloric acid, the oily acid extracted with ether, the ethereal solution rapidly dried, and the ether distilled off under diminished pressure. The residual pale yellow syrupy acid, which showed no tendency to crystallise, was at once analysed, and yielded numbers agreeing so well with those required by theory that there can be no doubt that the syrup consisted of practically pure 1-*methyl*cyclo*hexan-2-one-3-carboxylic acid.*

It is unfortunate that the yield of acid obtained by the above method of preparation is very small, and we have so far been unsuccessful in our attempts to discover better conditions. The following analyses were carried out with acid obtained from two preparations:

0·2451 gave 0·5535 CO_2 and 0·1755 H_2O. $C=61·6$; $H=8·0$.
0·1471 „ 0·3325 CO_2 „ 0·1042 H_2O. $C=61·7$; $H=7·9$.
$C_8H_{12}O_3$ requires $C=61·5$; $H=7·7$ per cent.

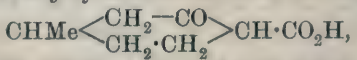
Ethyl 1-methyl*cyclo*hexan-2-one-3-carboxylate was obtained in a very small yield by leaving the syrupy keto-acid in contact with 5 per cent. alcoholic sulphuric acid for twenty-four hours. It was isolated in the usual manner (p. 1767), and distilled at about 125—130°/20 mm. (Found, $C=64·9$; $H=8·8$. Calc., $C=65·2$; $H=8·7$ per cent.)

Kötz and Michels (*Annalen*, 1906, **348**, 94), who obtained this ester by a different process (p. 1759), state that it distils at 115°/12 mm. We have also made a series of experiments on the reduction of 1-methyl*cyclo*hexan-2-one-3-carboxylic acid by sodium amalgam and sulphurous acid, using the conditions so successfully employed in other cases (p. 1765), but the product was always an almost colourless syrup, which could not be made to crystallise. That this syrup, which gave no coloration with ferric chloride, consisted of 1-*methyl*cyclo*hexan-2-ol-3-carboxylic acid*, is indicated by the following analysis:

0·1450 gave 0·3222 CO_2 and 0·1144 H_2O. $C=60·5$; $H=8·8$.
$C_8H_{14}O_3$ requires $C=60·8$; $H=8·9$ per cent.,

and the fact that the acid could not be obtained in a crystalline condition may be due, in part, to its being a mixture of stereoisomeric modifications.

dl- *and* d-1-*Methyl*cyclo*hexan-3-one-4-carboxylic Acid,*



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2{-}CO}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}>\mathrm{CH{\cdot}CO_2H},$$

and the corresponding 1-*Methyl*cyclo*hexan-3-ol-4-carboxylic Acids.*

dl-1-Methyl*cyclo*hexan-3-one-4-carboxylic acid was prepared from pure inactive 1-methyl*cyclo*hexan-3-one obtained from Kahlbaum.

The ketone (14 grams), dissolved in light petroleum, was mixed with powdered sodamide (5 grams), when rapid evolution of ammonia took place and the white sodium derivative separated. As soon as decomposition was complete, a rapid stream of dry carbon dioxide was passed, the whole being vigorously stirred during the operation.

The temperature rose rapidly to about 45° and then gradually subsided, and, as soon as the mass was quite cold, the stream of gas was interrupted. The product was treated with ice and hydrochloric acid in the usual manner, ether was then added, the ether-petroleum layer separated, extracted with sodium carbonate, and the alkaline solution acidified, when an oil separated, which rapidly crystallised.

The crystals were collected and purified by reprecipitation from the sodium salt, and then by crystallisation from ether:

0·1700 gave 0·3817 CO_2 and 0·1194 H_2O. C=61·2; H=7·3.

$C_8H_{12}O_3$ requires C=61·5; H=7·7 per cent.

dl-1-*Methyl*cyclo*hexan*-3-*one*-4-*carboxylic acid* separates from ether in prisms, and melts and decomposes at about 100—103°.

It is readily soluble in ether or alcohol, and moderately readily so in benzene or light petroleum, but it is rather sparingly soluble in cold water; the alcoholic solution gives with ferric chloride an intense violet coloration.

Ethyl dl-1-*methyl*cyclo*hexan*-3-*one*-4-*carboxylate* was prepared by leaving the acid in contact with a large excess of 5 per cent. alcoholic sulphuric acid for twenty-four hours, and then precipitating with water.

The oil was extracted with ether, the ethereal solution washed with sodium carbonate, dried, and fractionated, when practically the whole quantity distilled at 132—135°/24 mm., and gave an intense violet coloration when ferric chloride was added to the alcoholic solution:

0·1873 gave 0·4461 CO_2 and 0·1483 H_2O. C=64·9; H=8·8.

$C_{10}H_{16}O_3$ requires C=65·2; H=8·7 per cent.

dl-1-*Methyl*cyclo*hexan*-3-*ol*-4-*carboxylic acid*.—In preparing this acid, the pure *dl*-keto-acid (5 grams), dissolved in a slight excess of dilute sodium carbonate, was mixed with freshly prepared 3 per cent. sodium amalgam (500 grams) all at once, in an apparatus fitted with a mechanical stirrer, carbon dioxide being passed during the whole operation. The product was extracted in the usual manner, and again treated with sodium amalgam exactly as before, when an acid was obtained, which was at first oily, but gradually crystallised.

It was purified by crystallisation from ether, from which it separated in elongated prisms:

0·1412 gave 0·3132 CO_2 and 0·1120 H_2O. C=60·5; H=8·8.

$C_8H_{14}O_3$ requires C=60·8; H=8·8 per cent.

dl-1-*Methyl*cyclo*hexan*-3-*ol*-4-*carboxylic acid* melts at 130—131°, and is readily soluble in alcohol and moderately so in water, benzene, or chloroform. The alcoholic solution gives no coloration on the addition of ferric chloride.

d-1-*Methyl*cyclo*hexan*-3-*one*-4-*carboxylic Acid*.—The *d*-1-methyl*cyclo*hexan-3-one, employed in the preparation of this acid, was obtained from Schimmel & Co., and had been prepared from pulegone by hydrolysis (Wallach, *Annalen*, 1896, **289**, 339); it had $[\alpha]_D$ +8·8°.

This ketone was converted into *d*-1-methyl*cyclo*hexan-3-one-4-carboxylic acid in the manner already described in the case of the *dl*-acid, and the *d*-acid, thus obtained, separated from ether in small, and from light petroleum in large, prisms when the solutions in these solvents were allowed to concentrate slowly at the ordinary temperature:

0·1310 gave 0·2967 CO_2 and 0·0935 H_2O. C=61·3; H=7·8.
$C_8H_{12}O_3$ requires C=61·5; H=7·7 per cent.

The basicity was determined by titration with *N*/10-sodium hydroxide, when 0·3055 neutralised 0·0775 NaOH, whereas this amount of a monobasic acid, $C_8H_{12}O_3$, should neutralise 0·0784 NaOH.

d-1-*Methyl*cyclo*hexan*-3-*one*-4-*carboxylic acid* melts at about 102—103°, and gives a purple coloration when ferric chloride is added to its alcoholic solution.

0·4795, made up to 20 c.c. with alcohol, gave α_D +4·66° in a 2-dcm. tube at 17°, whence $[\alpha]_D$ +97·2°.

Several grams of the acid were heated in a small retort until decomposed, when it was found that the 1-methyl*cyclo*hexan-3-one which distilled over boiled at 169°, and had $[\alpha]_D$ +8·8°, showing that no change in rotation had occurred during the conversion into the acid and subsequent elimination of carbon dioxide. *Ethyl* d-1-*methyl*cyclo*hexan*-3-*one*-4-*carboxylate*, prepared in the same manner as the *dl*-ester, distilled at 134—137°/26 mm.:

0·2115 gave 0·5033 CO_2 and 0·1694 H_2O. C=64·9; H=8·9.
$C_{10}H_{16}O_3$ requires C=65·2; H=8·7 per cent.

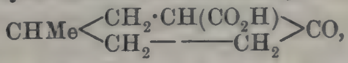
0·5423, made up to 25 c.c. with alcohol, gave α_D +3·49° in a 2-dcm. tube at 17·5°, whence $[\alpha]_D$ +84·16°.

d-1-*Methyl*cyclo*hexan*-3-*ol*-4-*carboxylic acid*, prepared by the reduction of the *d*-keto-acid with sodium amalgam exactly as described in the case of the *dl*-acid, melts at 129—130°:

0·1480 gave 0·3290 CO_2 and 0·1187 H_2O. C=60·6; H=8·8.
$C_8H_{14}O_3$ requires C=60·8; H=8·8 per cent.

0·1023, dissolved in alcohol and made up to 25 c.c., gave α_D −2·6° in a 2-dcm. tube at 17°, whence $[\alpha]_D$ −31·8°.

1-*Methyl*cyclo*hexan-4-one-3-carboxylic Acid,*



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH(CO_2H)}\\ \mathrm{CH_2{-}{-}{-}{-}CH_2}\end{matrix}{>}\mathrm{CO},$$

and its Reduction to 1-*Methyl*cyclo*hexan-4-ol-3-carboxylic Acid.*

1-Methyl*cyclo*hexan-4-one, obtained from Poulenc Frères, was found to contain methyl*cyclo*hexanol, and it was therefore purified by conversion into the sodium hydrogen sulphite derivative, and the regenerated ketone, which distilled at 169—170°, was employed in the following experiments. The conversion of the ketone into the carboxylic acid, by the action of sodamide and carbon dioxide, was carried out practically under the conditions which are described in detail in the case of the preparation of 1-methyl*cyclo*hexan-3-one-4-carboxylic acid (p. 1766). When the solution of the sodium salt was acidified, the acid was at once precipitated as a solid, and was readily purified by recrystallisation from ether, the pure acid being thus obtained in a yield of about 40 per cent. of that theoretically possible:

0·1110 gave 0·2500 CO_2 and 0·0780 H_2O. C=61·4; H=7·9.
0·1231 ,, 0·2769 CO_2 ,, 0·0860 H_2O. C=61·3; H=7·7.
$C_8H_{10}O_3$ requires C=61·5; H=7·7 per cent.

1-*Methyl*cyclo*hexan-4-one-3-carboxylic acid* separates from ether in prisms, and melts at 101°; it is readily soluble in alcohol, ether, or chloroform, but rather sparingly so in cold water; the addition of ferric chloride to the alcoholic solution produces a purple coloration which becomes rather bluer on the addition of a little water.

Ethyl 1-methyl*cyclo*hexan-4-one-3-carboxylate was prepared by leaving the finely divided acid (20 grams) in contact with excess of 5 per cent. alcoholic sulphuric acid (150 c.c.) for two days, and then precipitating with water. The ester was extracted with ether, the ethereal solution washed with sodium carbonate, dried, and distilled, when, after much methyl*cyclo*hexanone had passed over, the ester distilled at 128—130°/20 mm. (Found, C=65·5; H=8·9. Calc., C=65·2; H=8·7 per cent.)

Kötz and Michels (*Annalen*, 1906, **348**, 95) who obtained this ester by a different method (compare p. 1759), state that it distils at 110°/10 mm.

1-*Methyl*cyclo*hexan-4-ol-3-carboxylic acid* is obtained when the solution of the keto-acid in sodium carbonate is reduced by sodium amalgam at about 40—50° in an apparatus fitted with a mechanical stirrer, carbon dioxide being passed during the operation.

The product was acidified with dilute hydrochloric acid and repeatedly extracted with ether, the ethereal solution was dried and evaporated, when a syrupy acid remained, which gradually became semi-solid. After contact with porous porcelain for several days, the almost colourless, crystalline mass was recrystallised from ether:

0·1200 gave 0·2670 CO_2 and 0·0952 H_2O. C = 60·7; H = 8·9.

$C_8H_{14}O_3$ requires C = 60·8; H = 8·8 per cent.

1-*Methyl*cyclo*hexan*-4-*ol*-3-*carboxylic acid* separates from ether as a hard, crystalline crust and melts at 114°; it is readily soluble in water or alcohol, but sparingly so in cold ether.

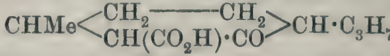
Ethyl 1-*Methyl*cyclo*hexan*-4-*ol*-3-*carboxylate.*—In preparing this ester, the porous plates used in the purification of the crude hydroxy-acid were extracted in a Soxhlet apparatus, and the syrupy extract was dissolved in a large excess of 10 per cent. alcoholic sulphuric acid. After several days, the product was mixed with water, the ester extracted with ether, the ethereal solution washed with sodium carbonate, dried, and evaporated, and the ester purified by fractionation, when it distilled constantly at 132—134°/17 mm.:

0·1083 gave 0·2559 CO_2 and 0·0977 H_2O. C = 64·4; H = 10·1.

$C_{10}H_{18}O_3$ requires C = 64·5; H = 9·7 per cent.

When this ester was hydrolysed by methyl-alcoholic potassium hydroxide, it yielded at once the hydroxy-acid in a crystalline form, and probably the best way of purifying this acid in future will be to convert the crude product of the reduction of the keto-acid at once into the ester, and, after distilling this, to regenerate the acid by hydrolysis.

d-iso*Menthonecarboxylic Acid*,



$$CHMe<\begin{matrix}CH_2\text{———}CH_2\\CH(CO_2H)\cdot CO\end{matrix}>CH\cdot C_3H_7.$$

In our first experiments on the behaviour of menthone on treatment with sodamide and carbon dioxide, the *l*-menthone employed had $[\alpha]_D$ −24·6°. This (20 grams) was dissolved in light petroleum and mixed with powdered sodamide (5 grams), when evolution of ammonia took place, and the soluble sodium derivative was readily produced.

A current of dry carbon dioxide was then passed through the solution for half an hour, without external cooling, and the product decomposed by ice and water. The aqueous layer was separated, acidified with hydrochloric acid, and, after saturating with ammonium sulphate, extracted with ether. The ethereal solution was shaken with cold sodium carbonate, the alkaline solution acidified, and well shaken with light petroleum (b. p. 40—60°), which extracts the monobasic acid. The extract was again treated with sodium carbonate, and the extraction with light petroleum repeated; finally the petroleum was distilled off under diminished pressure, the last traces being removed in a vacuum. The almost colourless syrup was at once analysed, with the following result:

0·1968 gave 0·4783 CO_2 and 0·1647 H_2O. C=66·3; H=9·3.

$C_{11}H_{18}O_3$ requires C=66·7; H=9·1 per cent.

0·6287, made up to 20 c.c. with alcohol, gave α_D +1·42° in a 2-dcm. tube at 16°, whence $[\alpha]_D$ +22·6°.

When the acid was distilled, it was readily decomposed with elimination of carbon dioxide, and the determination of the rotation of the *iso*menthone obtained gave the following result:

1·0268, made up to 20 c.c. with alcohol, gave α_D +1·95° in a 2-dcm. tube at 16°, whence $[\alpha]_D$ +19·0°.

A large number of similar experiments were made on the action of sodamide and carbon dioxide on various specimens both of *l*-menthone and of *d-iso*menthone, but, as the results of these are summarised in table I (p. 1762), it is unnecessary to give full details. One point of some interest may, however, be mentioned. In the first five experiments given in the table, the temperature was allowed to rise during the passage of the carbon dioxide through the solution of the sodium derivative in light petroleum, whereas, in the last two, which gave monocarboxylic acids of the highest rotations, the rise of temperature was prevented by surrounding the vessel containing the sodium derivative with ice. *d-iso*Menthonecarboxylic acid is an unstable substance, which slowly decomposes into *d-iso*menthone and carbon dioxide even at the ordinary temperature; its solution in alcohol gives with ferric chloride an intense purple coloration.

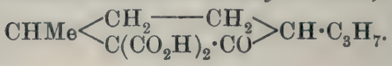
d-iso*Mentholcarboxylic acid* is produced when *d-iso*menthonecarboxylic acid (5 grams), dissolved in cold dilute sodium carbonate, is treated with 3 per cent. sodium amalgam (500 grams). The product was first extracted with ether in order to remove traces of neutral oil, then acidified, saturated with ammonium sulphate, and repeatedly extracted with ether. After drying and evaporating, a syrupy acid was obtained, which did not show any signs of crystallising, but that reduction had taken place was proved by the fact that the solution of the acid in alcohol did not give any coloration on the addition of ferric chloride:

0·2276 gave 0·5493 CO_2 and 0·2069 H_2O. C=65·8; H=10·1.

$C_{11}H_{20}O_3$ requires C=66·0; H=10·0 per cent.

0·4990, made up to 25 c.c. with alcohol, gave α_D +0·48° in a 2-dcm. tube at 16°, whence $[\alpha]_D$ +12·0°.

d-iso*Menthonedicarboxylic Acid*,



$$CHMe\left\langle\begin{matrix}CH_2\text{——}CH_2\\ C(CO_2H)_2\cdot CO\end{matrix}\right\rangle CH\cdot C_3H_7.$$

This acid is always produced along with the monocarboxylic acid when the conditions described in the last section are observed, and is extracted with ether after the removal of the monobasic acid.

The ethereal solution was shaken with a little sodium carbonate, and the acid precipitated, when it separated at first as an oil, which, however, rapidly crystallised. After the removal of traces of oily impurity by contact with porous porcelain and once crystallising from ether, the colourless mass melted at 121—128°.

By repeatedly crystallising from ether, a small quantity of the dibasic acid was obtained, which melted at 144°, but the loss during recrystallisation, due to elimination of carbon dioxide, was serious:

0·152 gave 0·3310 CO_2 and 0·1033 H_2O. C = 59·4; H = 7·5.

$C_{12}H_{18}O_5$ requires C = 59·5; H = 7·4 per cent.

0·3456, made up to 20 c.c. with alcohol, gave α_D + 4·3° in a 2-dcm. tube, whence $[\alpha]_D$ + 124·4°.

When this specimen was distilled, it yielded a *d-iso*menthone, of which the rotation was determined.

0·3662, made up to 20 c.c. with alcohol, gave α_D + 1·22° in a 2-dcm. tube at 17°, whence $[\alpha]_D$ + 33·3°.

d-iso*Menthonedicarboxylic acid* is readily soluble in alcohol or ethyl acetate, moderately so in acetone, chloroform, or water, and the alcoholic solution is not immediately coloured by the addition of ferric chloride. If the solution is kept, a faint violet coloration appears after some minutes, and this gradually deepens, a change which is doubtless due to the slow elimination of carbon dioxide and consequent formation of the monocarboxylic acid. Several specimens of this dicarboxylic acid were prepared from menthones of widely different rotations, and the results of these experiments are summarised in table II (p. 1762).

The authors are indebted to Dr. Lapworth for valuable suggestions made during the progress of this research, and they also wish to state that much of the expense was met by grants from the Research Fund of the Chemical Society.

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CLXXXVII.—cyclo*Hexane, its Separation from, and its Estimation in, Mixtures containing Benzene.*

By THOMAS STEWART PATTERSON and ALEXANDER FLECK.

WHEN *cyclo*hexane is prepared from benzene there is considerable difficulty both in separating the two substances by physical means, since their properties are so much alike, and in estimating the quantity of unchanged benzene in the product of reduction. It is usually recommended either to nitrate the benzene or to sulphonate it, but both processes are rather troublesome and are extravagant as regards time.

In connexion with the preparation, by the Sabatier-Senderens method, of a quantity of *cyclo*hexàne, the purity of which we had no ready means of ascertaining, it occurred to us that a simple method of analysis might possibly be based on an anticipated difference in the solvent influence on the rotation of ethyl tartrate, of benzene on the one hand, and *cyclo*hexane on the other, since it has been shown repeatedly that the optical activity of ethyl tartrate varies, often to a very great extent, in accordance with comparatively slightly differences in composition or constitution of the solvent.

Our proposal, therefore, was to make a solution in benzene and a solution in *cyclo*hexane of ethyl tartrate, and to determine the rotation of each. If there were a considerable difference, then the composition of a mixture of *cyclo*hexane and benzene could be ascertained by making an equally concentrated solution of ethyl tartrate in the mixture, measuring its rotation, and, by interpolation, estimating the relative proportions of its constituents.

We came across an unexpected but not unwelcome difficulty at the outset, when we found that *cyclo*hexane and ethyl tartrate are practically immiscible liquids, and therefore a very simple method of purification presented itself at once. When the quantity of benzene is small, the mixture need only be shaken up with about its own volume of ethyl tartrate, once or oftener, as seems necessary. When, however, benzene is present to the extent of about 50 per cent., some care must be exercised. Too much ethyl tartrate must not be used, or a homogeneous mixture will result. In connexion with the experiments quoted below, we found that four volumes of ethyl tartrate with one volume of benzene and one volume of *cyclo*hexane give a homogeneous mixture, but if only one volume of ethyl tartrate be used, the mixture separates into two layers. To test this method of separation, we made up a mixture of benzene and *cyclo*hexane in equal proportions. A quantity of this solution was shaken with half its volume of ethyl tartrate, and the whole cooled in a freezing mixture of ice and salt. The upper layer was then separated and shaken with about its own volume of ethyl tartrate, separated again, and distilled. Approximately 50 per cent. of the original *cyclo*hexane was recovered in a pure condition. If a mixture contains more than about 50 per cent. of benzene, its separation by shaking with ethyl tartrate would be distinctly more difficult, but could perhaps be accomplished by the addition of a little water to the mixture; we have not, however, attempted such a separation.

On account of this difficulty in regard to solubility, it was necessary to alter our proposed method of estimation in order to obtain an active liquid with which *cyclo*hexane would mix. We finally adopted a mixture of four volumes of ethyl tartrate and one volume of benzene, as we found that five volumes of this solution mix completely with one volume of *cyclo*hexane.

We therefore made up several solutions all containing 4 c.c. of ethyl tartrate and 1 c.c. of benzene (5 c.c. of a stock solution), and then one other c.c. of variable composition, either pure benzene, pure *cyclo*hexane, or a mixture of the two in known proportions. The rotation of each solution was then determined in a 50 mm. tube, the temperature being kept constant at 25°.

The results were as follows:

Volume percentage of *cyclo*hexane in the variable c.c.	0	20	40	60	80	100
$\alpha_D^{25°}$	+2·81°	2·58°	2·40°	2·21°	2·00°	1·76°
Deviation from mean	±0·00°	−0·02°	+0·015°	+0·03°	+0·03°	±0·00°

Thus a solution containing 4 vols. of ethyl tartrate and 2 vols. of benzene gives a rotation of +2·81°; one of 4 vols. of ethyl tartrate, 1 vol. of benzene, and 1 vol. of *cyclo*hexane gives a rotation of +1·76°. The substitution of 1 vol. of *cyclo*hexane for 1 vol. of benzene brings about therefore a diminution of 1·05° in rotation. Benzene has only a slight effect on the rotation of ethyl tartrate, so that *cyclo*hexane must have a considerable depressing influence, since a small proportion of it is capable of reducing the rotation of the above solution by about 33 per cent.

The total difference of 1·05° is, however, not very much to work upon, but since the polarimeter can be read to 0·01°, it should be possible, using great care, to reduce the error of an estimation by this method to about 1 per cent. By using larger quantities of substance and a longer polarimeter tube, an accuracy of 1 per cent. should not be difficult to attain to. If our data be plotted on a diagram, it will be seen that the intermediate values lie about the straight line* joining the two extremes. Assuming that the end values are correct, the maximum deviation from the straight line is +0·03°, whence these experiments may be relied on to about 3 per cent.

In order to test our method of analysis, one observer prepared a mixture of benzene and *cyclo*hexane, which was then examined by the other observer. One c.c. of the mixture was added to 5 c.c. of the stock solution. The rotation of this solution was +2·39°, which should correspond with 39·5 per cent. of *cyclo*hexane. The solution actually contained 35·7 per cent., so that the error was 3·8 per cent. The experiment had involved the use of a 1 c.c. pipette not used in the other set of observations, and this may account for the slightly increased error.

The product of our Sabatier-Senderens reaction was now shaken with about half its volume of ethyl tartrate. Some 90 to 92 per cent. of the preparation remained undissolved. This was separated and redistilled. Its boiling point was 80°. One c.c. of this was mixed with 5 c.c. of the stock solution of ethyl tartrate and benzene, and the resulting liquid examined as before in the polarimeter. It always happened—we tried the experiment several times—that the value of the rotation started about +1·90°, and fell gradually during a period of approximately eighteen hours to the value 1·75—1·76°, the latter being the rotation previously found for the solution containing 1 c.c. of pure *cyclo*hexane. These solutions were homogeneous, and, when placed in a freezing mixture, did not separate into two layers. The *cyclo*hexane was again shaken with ethyl tartrate, separated, and distilled, but the same behaviour as before was observed when its solution with benzene—ethyl tartrate was examined in the polarimeter. We are unable to suggest an explanation of this curious phenomenon. Solutions made up by mixing *cyclo*hexane (Kahlbaum) with ethyl tartrate and benzene did not show it.

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* In general, this would doubtless not be a straight line. See Trans., 1909, 95, 1131.

CLXXXVIII.—*The Identity of Osyritrin, Myrticolorin, Violaquercitrin, and Rutin.*

By Arthur George Perkin.

In a previous communication (Trans., 1902, **81**, 477) it was shown that osyritrin (*Osyris compressa*), myrticolorin (*Eucalyptus macroryncha*, Smith, Trans., 1898, **73**, 697), and violaquercitrin (*Viola tricolor*, Mandelin, *Jahresb.*, 1883, 1369) were identical, and the formula $C_{27}H_{28}O_{16}$ was assigned to these substances. From the products of their hydrolysis, quercetin and dextrose (as osazone) were isolated, and this decomposition was represented by the equation:

$$C_{27}H_{28}O_{16} + 3H_2O = C_{15}H_{10}O_7 + 2C_6H_{12}O_6.$$

The close resemblance of osyritrin to rutin was noted at the time, for it was pointed out that the dyeing properties of these glucosides are identical, and in an earlier paper (Trans., 1899, **75**, 440) that both compounds yield a monopotassium salt of similar character. On the other hand, as, according to Beilstein (*Handbuch*, 1897, III, 607), the formula of rutin was $C_{27}H_{32}O_{16},2H_2O$, its melting point above 190°, and the products of its hydrolysis quercetin and two molecules of rhamnose (Schunck, Trans., 1888, **53**, 264), it appeared unnecessary to carry out a further comparison of these two compounds. A more recent investigation by Schmidt (*Arch. Pharm.*, 1908, **246**, 214) and also by Wunderlich (*ibid.*, **246**, 224) has, however, shown that violaquercitrin is identical with rutin, and that, moreover, both compounds, when hydrolysed, give not only dextrose but rhamnose:

$$C_{27}H_{30}O_{16} + 3H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_6 + C_6H_{14}O_6.$$

From the fact of the identity of osyritrin, myrticolorin, and violaquercitrin, it was obvious that these three glucosides consisted of rutin, and a further examination of this point did not suggest itself. The appearance of a paper by Auld (Proc., 1910, **26**, 146) on the presence of osyritrin in the *Osyris abysinnica*, and a private communication from Dr. G. Clarke as to the existence of a substance apparently identical with osyritrin in the leaves of the *Tephrosia purpurea*, but which, however, on hydrolysis, gives quercetin, dextrose, and rhamnose, has shown that a further note on this subject is necessary.

Experiments have been therefore carried out to prove that when hydrolysed, myrticolorin and osyritrin give not only dextrose but rhamnose. Some quantity of the former was prepared in a pure condition from the residue of a commercial sample[*] received some time ago from Mr. H. G. Smith for a determination of its practical value, and this was digested with boiling dilute sulphuric acid in the usual manner. The filtrate from the quercetin was neutralised with barium carbonate, the clear liquid partly evaporated, and divided into two portions, the first of which was devoted to the preparation of osazone, and the second to the isolation of rhamnose.

The moist osazone washed with ether or acetone gave, as previously found, almost pure glucosazone, and it was owing to this procedure that the more soluble compound, considered to be an impurity, was previously not recognised. The crude substance dissolved in alcohol was now poured into about ten times its bulk of ether, and the solution thoroughly washed with water. By gentle evaporation, the main bulk of the glucosazone separated, and by further fractional distillation a more soluble compound was isolated, which, after purification, melted at 180—182°, and had the properties of rhamnosazone.

The second portion of the mixed sugar solution was treated with yeast, and when fermentation had ceased, the filtered liquid was evaporated to dryness. A concentrated alcoholic extract of the residue was inoculated with a crystal of rhamnose, and after two days deposited a considerable quantity of a colourless, crystalline substance. This was collected, washed with a mixture of ether and alcohol, and then melted at 92—93°, and this melting point was unaltered by its admixture with rhamnose itself.

For the examination of osyritrin, but 0·5 gram was available, and the preparation of crystalline rhamnose from this glucoside could not be attempted. The osazone of the mixed sugars isolated in the usual manner, however, yielded by fractional crystallisation from ether according to the method above described a substance melting at 180—183°, which was evidently rhamnosazone.

Finally, it was found that the melting points of osyritrin and myrticolorin were not affected by admixture with rutin. The formula $C_{27}H_{28}O_{16},3H_2O$, previously assigned to these preparations, should therefore be $C_{27}H_{30}O_{16},3H_2O$, and with this the analytical figures given are in equally good agreement.

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[*] The simplicity with which myrticolorin can be isolated from the *E. macrorryncha* in large quantity (Smith, *loc. cit.*) suggested a commercial possibility for this material. Although commercial trials have indicated that, especially on cotton, it is inferior to flavine (quercitrin), it is an excellent source of quercetin, and may eventually possess value in this respect.

CLXXXIX.—*Solubilities of Organic Substances in Organic Solvents: A Contribution to the Theory of Solubility.*

By Dan Tyrer.

In a previous paper (this vol., p. 621) on the solubility of salts above the critical point, it was shown that the solubility above this point varied with the density of the solvent, and could be represented as a function of the concentration of the solvent, that is, the amount of solvent contained in unit volume of the saturated solution. As the concentration of the solvent diminished, the solubility of the solute decreased. This suggests the idea that the concentration of the solvent is an important factor influencing the solubility of a solute. With rise of temperature, the concentration of a solvent in a saturated solution decreases, whereas the solubility of the solute usually increases. We must conclude from this that the solubility is influenced by a second factor, namely, temperature. Considering, then, the solubility of a particular solute in a particular solvent, we can say that the solubility under all possible conditions is governed by the following factors:

(1) Temperature;

(2) The concentration of the solvent;

or, expressed mathematically,

$$S = Kf(C).\phi(T),$$

where S is the solubility, C the concentration of the solvent, T the temperature, and K a constant.

The object of this work was to determine the form of the function $f(C)$.

It must be remarked that the above generalisations are independent of the mode or nature of the process of dissolution, and should be valid for all solutions. At the same time, however, if any comparison is to be made of the form of the function $f(C)$ for one solution with the form for another, the two solutions must be the same as regards their constitution. That is to say, there must be no polymerisation or association of the molecules of any kind in either of the solutions. For this reason, the solubilities of organic substances in organic solvents, in which the existence of molecular associations is improbable, have been investigated.

In the majority of aqueous solutions, and probably in all solutions where the solvent is an associated liquid, as, for example, a solvent containing a hydroxyl group, molecular association of the solvent and solute undoubtedly occurs, and the process of dissolution in these cases is probably due to some extent to the formation of these complex molecules. With non-associated solvents, there is evidence for the belief that the solute (if it is also non-associated) does not associate with the solvent, but the molecules of both move freely among each other like the molecules in a mixed gas.

Forch (*Ann. Physik*, 1905, [iv], **17**, 1012) found that naphthalene dissolved in non-associated solvents had a constant molecular volume at constant temperature independent of the solvent or the concentration. Such a regularity as this would not exist were there any appreciable molecular association in these solutions. Furthermore, in contrast with associated liquids, when two non-associated liquids are mixed, very small volume and temperature changes occur (Linebarger, *Amer. Chem. J.*, 1896, **18**, 440; Brown, Trans., 1881, **39**, 202; Thorpe and Rodger, Trans., 1897, **71**, 367; Walker and Henderson, *Trans. Roy. Soc. Canada*, 1902, [ii], **8**, Sect. iii, 105). This can only be regarded as indicating that no molecular association occurs when non-associated substances are mixed.

From theoretical considerations regarding the form of the composition—partial pressure curve of a constituent of a binary mixture of liquids—Dolezalek (*Zeitsch. physikal. Chem.*, 1908, **64**, 727) concluded, from existing data, that in binary mixtures of such liquids as benzene, toluene, chloroform, and in general liquids which are not associated in a pure state, there is no association or polymerisation of any kind.

In order therefore that any regularities which might exist would not be concealed by complications arising from molecular associations, it was necessary to study solubilities of non-associating organic solutes in non-associating organic solvents. General experience leads us to believe that such substances are those not containing hydroxyl, amino-, or cyano-groups. Except in the case of solutions above the critical point, where the concentration of the solvent can be varied at will, only one method of attacking the problem seems available. A solute satisfying the above conditions is found which is soluble in a solvent A, and very slightly soluble (compared with solubility in A) in another solvent B, which is completely miscible with A. B is then used to dilute A, and solubilities in mixtures of A and B in varying proportions from pure A to pure B determined at constant temperature. A determination of the density of the saturated solution is also necessary in order to calculate the concentration of each of the solvents.

An approximation is then made by supposing the amount of the solute dissolved by the B portion of the mixture to be proportional to the concentration of the solvent B. This amount subtracted from the total amount dissolved by the mixture gives the amount dissolved by A alone. Any error thus introduced will be negligibly small if there is a considerable difference in the solubilities in the respective pure solvents except at low concentrations of A. It must be pointed out that the assumption is here made that the solvent B has no other effect than that of merely diluting A. The necessary conditions greatly restrict the number of cases open to investigation, and only one class of liquids has been found which can be used as diluents. These are the aliphatic hydrocarbons, in which, as a general rule, organic substances of the above specified nature are much less soluble than in other organic solvents.

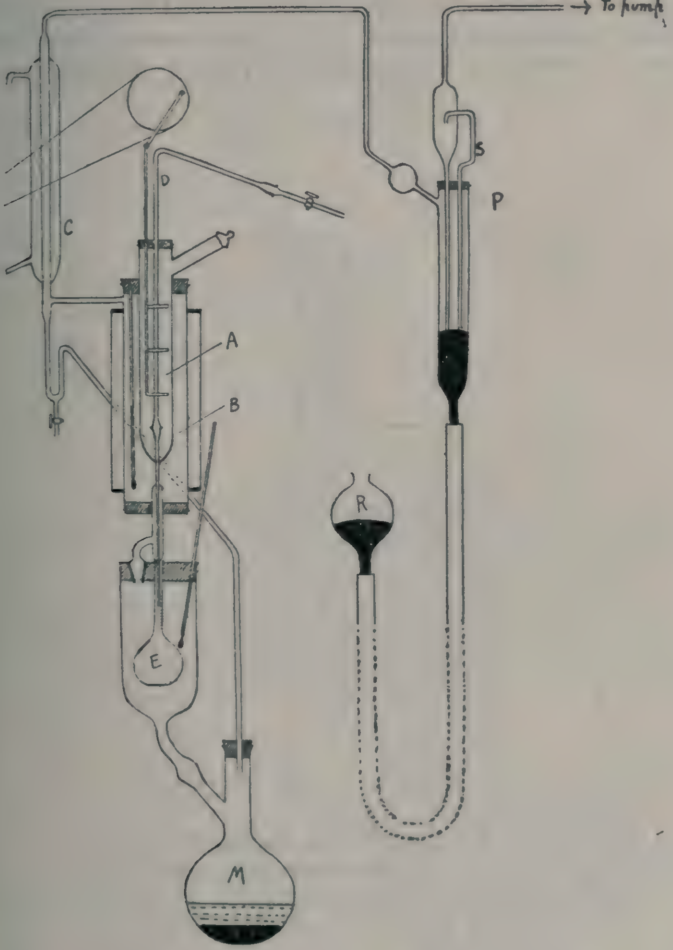
Incidentally, some careful measurements of the solubility of some organic substances in organic solvents at varying temperatures have been made.

Apparatus.

As it was necessary to determine the concentration of the solvent in the saturated solution besides the solubility of the solute, the ordinary type of solubility apparatus was not suitable, and a special form had to be devised. This is best explained by reference to Fig. 1.

The solvent with excess of the solute (in not too fine a powder) is placed in the inner tube *A* and well mixed together with a vertically acting stirrer worked by a small motor. The tube *A* is surrounded by a bath of vapour, which circulates through the cylinder *B*, condenses in *C*, and returns to the boiling flask *M*. When the solution is saturated, it is allowed to settle, and the clear solution run out (by raising the tube *D*) into a small graduated flask *E*, which is maintained at the same temperature as the solution in *A*. The temperature of the vapour-bath is varied by changing the pressure under which the liquid in the flask *M* is boiling. For this purpose the top of the condenser *C* is attached to a water pump, and the pressure can be maintained perfectly constant by a manostat *P*. The level of the mercury column in *P* must necessarily remain constant about the end of the tube *S*. The pressure, and consequently the temperature of the bath, can be varied at will by merely raising or lowering the mercury reservoir *R*. The temperature can with care be maintained constant to 0·01°. For this purpose the apparatus must be quite air-tight, the liquid in the boiling flask must not bump (which is entirely prevented by placing in the flask a layer of mercury), and a pure boiling liquid must be used. The density of the saturated solution (and from this the concentration of the solvent can be calculated) is found by weighing the bottle *E* filled up to the graduation on the neck with the saturated solution. The volume of this bottle had previously been determined with great care, and corrections made for expansion of the glass, curved surface of meniscus, etc. After being weighed, the contents (and washings) of the bottle *E* are poured into a special form of evaporating bottle (Fig. 2). The body of this bottle is immersed in a water-bath kept at a temperature too low for any escape by volatilisation of the dissolved substance, and the evaporation carried out by drawing over the surface a rapid current of dry air.

Fig. 1.



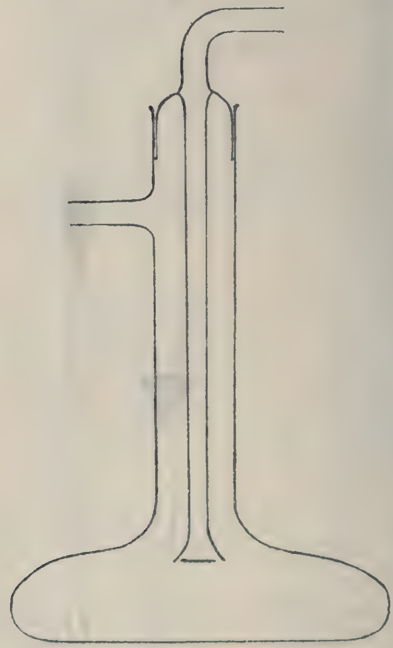
Two thermometers graduated in fifths of a degree, and readable to 1/50th of a degree, were used, one in the lower portion of the apparatus, and the other in the higher portion.

Kahlbaum's chemicals were used without any further purification.

Results.

The values given in the tables below were read from the smoothed curves of experimental results, which, in the case of the solubility determinations in the pure solvents at varying temperatures, were made every 5° or 6°. The lowest temperatures (10°—13°) were obtained by substituting for the vapour-bath a current of cold water at constant temperature. The results for 0° were obtained by extrapolation, and are probably a little less accurate than the other figures. The probable error in the values given for the solubilities in the pure solvents is about ±0·001 to ±0·002, whilst the figures for the concentration of the solvent are accurate to about 0·0002 gram per c.c.

FIG. 2.



Solubility of Anthraquinone in Benzene.

Temperature.	Solubility in grams per 100 grams of solvent.	Concentration of solvent in grams per c.c.
0°	0·110	0·8986
10	0·173	0·8880
20	0·256	0·8771
30	0·350	0·8658
40	0·495	0·8543
50	0·700	0·8429
60	0·974	0·8310
70	1·355	0·8180
80	1·775	0·8044

Solubility of Anthraquinone in Chloroform.

Temperature.	Solubility in grams per 100 grams of solvent.	Concentration of solvent in grams per c.c.
0°	0·340	1·5180
10	0·457	1·4975
20	0·605	1·4765
30	0·780	1·4545
40	0·994	1·4315
50	1·256	1·4086
55	1·415	1·3967
60	1·577	1·3847

Solubility of Anthracene in Benzene.

Temperature.	Solubility in grams per 100 grams of solvent.	Concentration of solvent in grams per c.c.
0°	0·605	0·8940
10	0·975	0·8820
20	1·43	0·8686
30	2·03	0·8547
40	2·78	0·8394
50	3·75	0·8234
60	5·14	0·8070
70	7·00	0·7876
75	8·35	0·7772

The values for the solubility in the above table are accurate to the last decimal figure given. They differ rather considerably, however, from values given by Findlay (Trans., 1902, **81**, 1221). Most of Findlay's values were not experimentally determined, but calculated by aid of a theoretical expression enabling the comparison of one solubility curve with another. His results for the higher temperatures are undoubtedly much too low, and those for lower temperatures too high.

Solubility of Phenanthraquinone in Benzene.

Temperature.	Solubility in grams per 100 grams of solvent.	Concentration of solvent in grams per c.c.
10°	0·412	0·8867
15	0·471	0·8807
20	0·538	0·8750
30	0·738	0·8633
40	1·032	0·8514
50	1·354	0·8390
60	1·760	0·8263
70	2·687	0·8112
80	3·770	0·7950

Solubility of Phenanthraquinone in Ethyl Acetate.

Temperature.	Solubility in grams per 100 grams of solvent.	Concentration of solvent in grams per c.c.
10°	0·518	0·9092
20	0·626	0·8969
30	0·770	0·8840
40	0·995	0·8707
50	1·292	0·8567
55	1·457	0·8493
60	1·640	0·8423
65	1·902	0·8348
70	2·215	0·8270
75	2·515	0·8188

An interesting point about the above figures is that the concentration of the solvent in the saturated solution is very approximately a linear function of the temperature. For example, the concentration of a saturated solution of phenanthraquinone in benzene is given approximately by the equation:

$$C = 0{\cdot}8986 - 0{\cdot}00119t,$$

where t is the temperature in degrees centigrade. Introducing this approximation into the fundamental equation, we can write:

$$S = K.f(a - bt).\phi(t),$$

where a and b are constants. This gives the solubility in terms of the temperature.

Solubility of Anthraquinone in Chloroform diluted with Hexane at 12·6°.

The solubility in the hexane alone at 12·6° is 0·006 per cent., and in the chloroform alone 0·482 per cent. This difference is sufficiently great to justify the supposition that the amount dissolved by the hexane alone in the mixture is proportional to the concentration of the hexane. The values of the solubility in the following table have been found by determining the solubility in the mixed solvent and subtracting for the amount dissolved by the hexane alone. The values for the smaller concentrations are only approximate, for the error of the above approximation is here greatest. The solubilities for the concentration of 1·5000 grams per c.c., given in all the chloroform solutions, were found by extrapolation, as the concentration of pure chloroform is below this value.

Concentration of solvent in grams per c.c.	Solubility in grams per 100 of solvent.	Concentration of solvent in grams per c.c.	Solubility in grams per 100 of solvent.
0·0	0·0	0·9000	0·255
0·1500	0·036	1·0500	0·305
0·3000	0·077	1·2000	0·358
0·4500	0·120	1·3500	0·420
0·6000	0·163	1·5000	0·507
0·7500	0·210		

Solubility of Anthraquinone in Chloroform diluted with Hexane at 49°.

In this case the solubility in the chloroform alone is about twenty-two times greater than that in the hexane.

Concentration of solvent in grams per c.c.	Solubility in grams per 100 of solvent.	Concentration of solvent in grams per c.c.	Solubility in grams per 100 of solvent.
0·0	0·0	0·9000	0·730
0·1500	0·123	1·0500	0·857
0·3000	0·241	1·2000	1·000
0·4500	0·363	1·3500	1·144
0·6000	0·483	1·5000	1·297
0·7500	0·608		

Solubility of Phenanthraquinone in Chloroform diluted with Pentane at 14·5°.

In this case the solubility in the chloroform alone is about seventy times greater than that in the pentane.

Concentration of solvent in grams per c.c.	Solubility in grams per 100 of solvent.	Concentration of solvent in grams per c.c.	Solubility in grams per 100 of solvent.
0·500	0·390	1·300	1·920
0·700	0·603	1·400	2·250
0·900	0·885	1·500	2·580
1·100	1·290		

Solubility of Phenanthraquinone in Benzene diluted with Pentane at 15·5°.

0·0	0·0	0·500	0·258
0·100	0·037	0·600	0·317
0·200	0·082	0·700	0·375
0·300	0·133	0·800	0·435
0·400	0·195		

Solubility of Phenanthraquinone in Ethyl Acetate diluted with a Mixture of Hydrocarbons from Petroleum at 48°.

As a diluent, a mixture of hydrocarbons boiling between 82° and 92°, distilled from petroleum, was used. The solubility in the acetic ester alone is about eighteen times greater than in the mixture of hydrocarbons.

Concentration of solvent in grams per c.c.	Solubility in grams per 100 of solvent.	Concentration of solvent in grams per c.c.	Solubility in grams per 100 of solvent.
0·200	0·617	0·600	1·096
0·300	0·775	0·700	1·173
0·400	0·913	0·800	1·212
0·500	1·015	0·900	1·243

Solubility of Phenanthraquinone in Benzene diluted with a Mixture of Hydrocarbons from Petroleum at 48°.

Concentration of benzene in grams per c.c.	Solubility in grams per 100 of solvent.	Concentration of benzene in grams per c.c.	Solubility in grams per 100 of solvent.
0·0	0·0	0·500	0·742
0·100	0·140	0·600	0·888
0·200	0·290	0·700	1·036
0·300	0·440	0·800	1·194
0·400	0·593	0·850	1·300

Solubility of Benzil in Benzene diluted with Hexane at 12·3°.

The solubility in the benzene is about fifty times greater than in the hexane.

0·0	0·0	0·500	24·8
0·200	9·0	0·600	32·8
0·300	13·2	0·700	39·9
0·400	18·3		

Conclusions.

The results given in the above tables have been plotted graphically (see Fig. 3). The curves given are not all on the same scale, but still they serve to indicate the general form of the relation between the solvent-concentration and the solubility. It will be observed that the cases studied do not give a common type of curve as was at first expected. This means that the law governing the relation between the solubility and the concentration of the solvent is not general, but is dependent on the nature of the substances. Several of the cases do, however, give curves which approximately represent the solubility as a linear function of the concentration of the solvent. In the case of phenanthraquinone in benzene at 48°, for example (curve C), the solubility is given fairly closely by the simple relation, $S = 1{\cdot}48C$, where S is the solubility and C the solvent-concentration. Phenanthraquinone in benzene at 15·5°, and anthraquinone in chloroform at 49° and at 12·6° approximate rather less closely to the linear function. The other cases, however, can only be represented accurately by an equation of the form:

$$S = aC + bC^2 + cC^3,$$

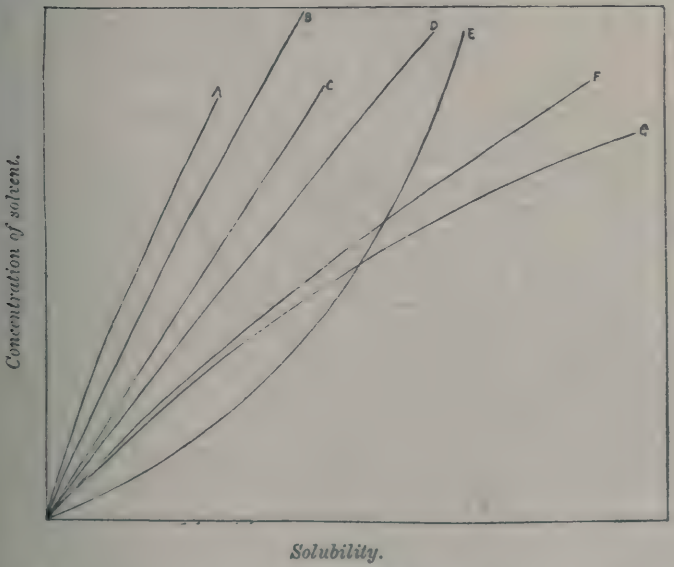
where a, b, and c are constants.

There is a possibility that in the case of phenanthraquinone in acetic ester (curve E), molecular association occurs, and this would be sufficient to explain the exceptional nature of the curve. In support of this, it may be mentioned that Möller (*Zeitsch. physikal.*

Chem., 1909, **69**, 449) finds that in a mixture of carbon tetrachloride and acetic ester a large proportion of the latter exists as double molecules.

With a mixture of associated solvents, we might expect to obtain very irregular curves through the formation of complex molecules. Holleman and Antusch (*Rec. trav. chim.*, 1894, **13**, 277), working with a mixture of ethyl alcohol and water, and with organic solutes which are much more soluble in the former than in the latter, found in many cases (acetanilide, acetonaphthalide, benzamide, etc.) that the solubility in the mixed solvent, starting from pure alcohol, increased at first as the proportion of the water in the mixture increased, reached a maximum, and then decreased. Herz and Knoch (*Zeitsch. anorg. Chem.*, 1904, **41**, 315) found that succinic acid dissolved in a mixture of acetone and water gave a similar maximum solubility.

FIG. 3.



A. Phenanthraquinone in benzene at 15·5° (diluent: pentane).
B. Anthraquinone in chloroform at 12·6° (diluent: hexane).
C. Phenanthraquinone in benzene at 48° (diluent: mixture of hydrocarbons).
D. Anthraquinone in chloroform at 49° (diluent: hexane).
E. Phenanthraquinone in ethyl acetate at 48° (diluent: hydrocarbons).
F. Benzil in benzene at 12·3° (diluent: hexane).
G. Phenanthraquinone in chloroform at 14·5° (diluent: pentane).

The existence of these maxima can only be explained on the supposition that associated molecules are formed with the two solvents which have a greater solvent action on the particular solutes than have the pure solvents.

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CXC.—*A New Method for the Preparation of Aryl Ethers of Glycerol α-Monochlorohydrin.*

By DAVID RUNCIMAN BOYD and ERNEST ROBERT MARLE.

IN the preparation of glycide aryl ethers by the action of epichlorohydrin on a solution of a phenol in excess of sodium hydroxide (Trans., 1908, **93**, 838; 1909, **95**, 1808), we have invariably observed amongst the products of the reaction a small quantity of a compound containing chlorine, which we assumed to be the glycerol α-monochlorohydrin aryl ether, $Ar\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2Cl$.

This fact led us to investigate whether sodium hydroxide might be advantageously employed as a catalytic agent to bring about the addition of a phenol to epichlorohydrin. We find that this is so. In the presence of a small quantity of sodium hydroxide, epichlorohydrin and phenol react at the ordinary temperature with moderate rapidity to form γ-chloro-β-hydroxy-α-phenoxypropane. From a mixture of 94 grams of phenol and 92·5 grams of epichlorohydrin, to which 0·5 gram of sodium hydroxide had been added, we obtained, after the mixture had been kept for about three weeks, 66 grams of chlorohydrin ether, boiling at 151—160°/18 mm.; from this, on fractionation, 49 grams, boiling at 155—156°/16 mm., were obtained.

Fischer and Krämer (*Ber.*, 1908, **41**, 2728), following the method of Lindemann (*Ber.*, 1891, **24**, 2145), have prepared the phenyl ether (γ-chloro-β-hydroxy-α-phenoxypropane) by heating epichlorohydrin with phenol in a closed vessel for forty hours at 160°. They give 152—153°/12 mm. as the boiling point of the pure substance. They obtained, from 500 grams of epichlorohydrin and 600 grams of phenol, 173 grams of crude ether, boiling at 135—155°/12 mm.; the yield of the pure compound is not mentioned.

Fourneau (*J. Pharm. Chim.*, 1910, [vii], **1**, 58) gives 25 to 30 grams as the yield of chlorohydrin ether obtained from 65 grams of phenol by the same method, but no boiling point is mentioned.

Fourneau (*loc. cit.*) has also prepared γ-chloro-β-hydroxy-α-phenoxypropane by boiling phenol with a large excess of epichlorohydrin. The yield mentioned is 20 to 22 grams from 35 grams of phenol, but no information is given with regard to the purity of this product. The boiling point given by Fourneau for the pure substance, 170°/21 mm., appears to be considerably too high.

Using Lindemann's method, and heating for ten hours at 150°, we have obtained about 5 grams of γ-chloro-β-hydroxy-α-phenoxypropane, boiling at 152—155°/12 mm., from 47 grams of phenol. We were unable to detect the presence of any phenyl glycide ether, which, according to Lindemann, is one of the products formed when epichlorohydrin is heated with phenol.

EXPERIMENTAL.

γ-Chloro-β-hydroxy-α-phenoxypropane, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl$.

Half a gram of sodium hydroxide (1/80 mol.), dissolved in about 5 c.c. of water, was added to a mixture of 94 grams of phenol (1 mol.) and 92·5 grams of epichlorohydrin (1 mol.). The mixture formed a clear solution. After it had been kept for about three weeks at the laboratory temperature, it had still a strongly alkaline reaction. It was then treated with ether; the ethereal solution was shaken with dilute sodium hydroxide solution to remove unchanged phenol, and dried over potassium carbonate. On distillation of the product under diminished pressure, 66 grams of γ-chloro-β-hydroxy-α-phenoxypropane, boiling at 151—160°/18 mm., were obtained. The residue in the distilling flask was very small in amount. Fractional distillation of the crude ether gave 49 grams of oil, boiling at 155—156°/16 mm. The portion analysed boiled at 156°/16 mm. (Found, $C=57·90$; $H=6·11$; $Cl=18·85$. Calc., $C=57·89$; $H=5·94$; $Cl=19·01$ per cent.) Prepared in this way, the ether forms a colourless, somewhat viscous oil, with a scarcely noticeable odour. On treatment with solid potassium hydroxide, it is converted into phenyl glycide ether.

The *phenylurethane*, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH(O{\cdot}CO{\cdot}NH{\cdot}C_6H_5){\cdot}CH_2Cl$, was prepared by keeping a mixture of the chlorohydrin ether and phenyl *iso*cyanate for twelve days at the ordinary temperature. The solid mass obtained was treated with warm alcohol. The alcoholic solution was filtered, and the *phenylurethane*, obtained on evaporation of the alcohol, was crystallised several times from light petroleum. It forms needles, melting at 70°:

0·2351 gave 0·1111 AgCl. $Cl=11·69$.

0·4131 „ 16·65 c.c. N_2 (moist) at 20° and 740 mm. $N=4·49$.

$C_{16}H_{16}O_3NCl$ requires $Cl=11·60$; $N=4·58$ per cent.

γ-*Chloro-β-hydroxy-α-*o*-tolyloxypropane,* $C_7H_7{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl$.

This substance was prepared by the same method as that employed for the phenyl ether. Fifty-four grams of *o*-cresol (1 mol.), 46 grams of epichlorohydrin (1 mol.), and 0·5 gram of sodium hydroxide (1/40 mol.) were used. After nine days the mixture was still strongly alkaline. The yield of crude substance, boiling at 169—172°/22 mm., was 25 grams. The pure ether forms a colourless, somewhat viscous oil, boiling at 166°/18 mm.:

0·2278 gave 0·1627 AgCl. Cl = 17·67.
$C_{10}H_{13}O_2Cl$ requires Cl = 17·68 per cent.

The *phenylurethane*, $C_7H_7{\cdot}O{\cdot}CH_2{\cdot}CH(O{\cdot}CO{\cdot}NH{\cdot}C_6H_5){\cdot}CH_2Cl$, prepared as in the previous case, crystallised from a solution in cold alcohol, on addition of a little water, in needles, melting at 81—82°:

0·2715 gave 0·1203 AgCl. Cl = 10·96.
0·2843 ,, 10·9 c.c. N_2 (moist) at 20° and 744 mm. N = 4·29.
$C_{17}H_{18}O_3NCl$ requires Cl = 11·09; N = 4·38 per cent.

γ-*Chloro-β-hydroxy-α-*p*-tolyloxypropane,* $C_7H_7{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl$.

Fifty-seven grams of *p*-cresol, 46 grams of epichlorohydrin, and 1 gram of sodium hydroxide were used, and the mixture was kept for eight days. The yield of crude substance, boiling at 178—183°/30 mm., was 47·5 grams. The pure ether boils at 165°/14 mm., and forms a colourless, rather viscous oil:

0·2036 gave 0·1447 AgCl. Cl = 17·58.
$C_{10}H_{13}O_2Cl$ requires Cl = 17·68 per cent.

The *phenylurethane*, $C_7H_7{\cdot}O{\cdot}CH_2{\cdot}CH(O{\cdot}CO{\cdot}NH{\cdot}C_6H_5){\cdot}CH_2Cl$, prepared as in the previous cases, crystallised from alcohol in needles, melting at 113—114°:

0·2349 gave 0·1051 AgCl. Cl = 11·06.
0·3017 ,, 11·6 c.c. N_2 (moist) at 17·5° and 751 mm. N = 4·40.
$C_{17}H_{18}O_3NCl$ requires Cl = 11·09; N = 4·38 per cent.

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CXCI.—*The Action of Ammonia on the Glycide Aryl Ethers. Part II. Phenoxypropanolamines.*

By DAVID RUNCIMAN BOYD.

IN a previous communication (Boyd and Knowlton, Trans., 1909, **95**, 1802) an account was given of the bases obtained by the action of ammonia on *o*-tolyl glycide ether. From analogy to other cases, it was considered probable that in this reaction the amino-group becomes attached to the α-carbon atom of the *o*-tolyl glycide ether, giving a primary base of the formula

$$C_7H_7 \cdot O \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot NH_2.$$

This view has now been confirmed by the preparation of the same base from γ-chloro-β-hydroxy-α-*o*-tolyloxypropane,

$$C_7H_7 \cdot O \cdot CH_2 \cdot CH(OH) \cdot CH_2Cl,$$

and ammonia.

The action of ammonia on phenyl glycide ether has also been studied, and bases similar in character to those resulting from *o*-tolyl glycide ether have been obtained.

This reaction has also been investigated recently by Fourneau, who states (*J. Pharm. Chim.*, 1910, [vii], **1**, 99) that phenyl glycide ether and γ-chloro-β-hydroxy-α-phenoxypropane react with ammonia to produce a secondary base only, and who appears to regard such behaviour as typical of the aromatic and higher fatty halogen-hydrins. It is obvious, however, that the relative quantities of primary, secondary, and tertiary bases obtained in such a reaction as that under consideration must depend very largely on the conditions of the experiment. If, for instance, the glycide ether is dissolved in a considerable volume of a strong solution of ammonia in 50 per cent. alcohol, the principal product is the primary base.

EXPERIMENTAL.

β-*Amino-β′-phenoxy*iso*propyl Alcohol*,
$$C_6H_5 \cdot O \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot NH_2.$$

The *hydrochloride* of this base was prepared by the method already described in connexion with the corresponding *o*-tolyloxy-compound (*loc. cit.*). In one experiment, using 38 grams of phenyl glycide ether, 200 c.c. of concentrated aqueous ammonia, and 180 c.c. of alcohol, and keeping the mixture for some days at the ordinary temperature, about 30 grams of the hydrochloride were obtained. The salt resembles the corresponding *o*-tolyloxy-compound in having no definite melting point. It softens at 136°, but is not completely melted until about 228°. It dissolves very easily in cold water.

The free base separated in rosettes of small needles on adding sodium hydroxide to a concentrated aqueous solution of the hydrochloride. After washing with water and drying in a desiccator over potassium hydroxide, it melted at 97—98°:

0·1727 gave 0·4092 CO_2 and 0·1204 H_2O. C = 64·62; H = 7·81.
0·1982 „ 14·2 c.c. N_2 (moist) at 12° and 761 mm. N = 8·52.
$C_9H_{13}O_2N$ requires C = 64·62; H = 7·85; N = 8·38 per cent.

The base is easily soluble in water, giving a solution with a strongly alkaline reaction; it is less soluble in water containing sodium hydroxide.

The *platinichloride* melts and decomposes at 201°:

0·3066 gave 0·0804 Pt. Pt = 26·22.
$(C_9H_{13}O_2N)_2,H_2PtCl_6$ requires Pt = 26·21 per cent.

The *benzoate* crystallises from alcohol in prisms, which soften at 140°, and melt at 143°:

0·2560 gave 10·9 c.c. N_2 (moist) at 17° and 747 mm. N = 4·82.
$C_9H_{13}O_2N,C_7H_6O_2$ requires N = 4·84 per cent.

β-Amino-β′-phenoxy*iso*propyl alcohol can also be prepared by treating γ-chloro-β-hydroxy-α-phenoxypropane with a solution of ammonia in 50 per cent. alcohol. The method of procedure is practically the same as when the glycide ether is employed, except that after the alcohol and ammonia have been expelled, it is necessary to add some dilute hydrochloric acid in order to precipitate the hydrochloride of the secondary base, which otherwise would remain to some extent in solution along with the salt of the primary amine.

Dihydroxydiphenoxydipropylamine, $[C_6H_5\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2]_2NH$.

A secondary base, melting at 97—98°, and giving a hydrochloride melting at 175°, has been described by Fourneau (*loc. cit.*) as the product obtained by heating γ-chloro-β-hydroxy-α-phenoxypropane with aqueous ammonia.

The crude product obtained from phenyl glycide ether and ammonia, which melted about 97°, was washed twice with ether, and then treated with hydrochloric acid. After several crystallisations from dilute alcohol, the hydrochloride softened at 169°, and melted at 171—172°. (Found, Cl = 9·89. Calc., Cl = 10·03 per cent.) The salt is moderately soluble in cold water, but only very sparingly so in water containing hydrochloric acid.

The free base was obtained by adding sodium hydroxide to a solution of the hydrochloride in boiling dilute alcohol. After two crystallisations from alcohol, it melted almost completely at 101—102°, but fusion was not quite complete until 104°. Since the nitrogen estimation gave a result in satisfactory agreement with the figure required for a secondary base, it seems possible that the want of sharpness in the melting point may be due to the presence of both of the two possible stereoisomerides. (Found, N=4·46. Calc., N=4·42 per cent.)

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CXCII.—*The Resolution of Benzoyloscine.*

By Frank Tutin.

The base oscine (scopoline), $C_8H_{13}O_2N$, formed by the hydrolysis of the alkaloid hyoscine (scopolamine), is generally acknowledged to be closely related structurally to tropine, $C_8H_{15}ON$, although its constitution is not known. Tropine, which contains two similar asymmetric carbon atoms, has recently been examined from a stereochemical point of view by M. Barrowcliff and the present author (Trans., 1909, **95**, 1966), and found to be an internally compensated compound. It was therefore considered of interest to investigate oscine in the same direction, particularly as the evidence so obtained might be of service in assigning a constitutional formula to this compound.

Oscine was prepared from *l*-hyoscine, and examined polarimetrically, when it was found to be optically inactive. As the amount of material prepared was not large, the base was converted into its benzoyl derivative before attempting its resolution, thereby increasing the size of the molecule. Moreover, the salts of benzoyloscine crystallise more readily than those of the original base.

Benzoyloscine d-*camphorsulphonate* (m. p. 167—168°) was first prepared, but, although this salt was submitted to a prolonged fractional crystallisation, no evidence of resolution could be obtained. When, however, *benzoyloscine* d-*bromocamphorsulphonate* was fractionally crystallised, it was at once seen that a separation was being effected, and, after three fractionations, *benzoyl*-d-*oscine* d-*bromocamphorsulphonate* (m. p. 246°) was obtained in a state of purity. This salt had $[\alpha]_D$ +51·9° in aqueous solution, from which it is calculated that the basic ion has $[\alpha]_D$ +10·0°. The *base* obtained from this salt, when examined in 50 per cent. alcohol, had

$[\alpha]_D + 3{\cdot}5°$. In order further to characterise this optically active base, several salts were prepared from it, each of which was found to melt at a higher temperature than the corresponding salt of the inactive base, as will be seen from the following table:

Name of salt	M. p. of salt of *dl*-base.	M. p. of salt of *d*-base.
Hydrochloride	266°	283—284°
Nitrate	195	200°
Picrate	185	211—212
Aurichloride	183—194	189—190

d-*Oscine* could not be obtained from benzoyl-*d*-oscine by hydrolysis with an alkali, since racemisation rapidly occurred under these conditions. Recourse was therefore had to acid hydrolysis, the liberated benzoic acid being removed by means of steam. A solution containing d-*oscine hydrochloride* was thus obtained, by means of which an approximate determination of the optical rotatory power of *d*-oscine was made, when the value $[\alpha]_D + 77{\cdot}7°$ was found.

Attempts to obtain *benzoyl*-l-*oscine* d-*bromocamphorsulphonate* in a state of purity were unsuccessful.

It is evident from the results given in this paper that oscine is capable of resolution into two stereoisomerides, and no evidence of the existence of more than two such compounds was obtained. Any structural formula which may be assigned to this base must therefore contain either one or two asymmetric carbon atoms, but, if the latter be the case, both the asymmetric groupings must be similar.

EXPERIMENTAL.

About five grams of *l*-hyoscine (scopolamine) were heated for several hours on a water-bath with a large excess of alcoholic potassium hydroxide. Water was then added, and the resulting oscine (scopoline) extracted with chloroform, after which it was purified by distillation, when it passed over at 240—245°. The solid so obtained, which was optically inactive, was treated with a large excess of benzoyl chloride, when an additive *compound* of the base and the acid chloride was first formed. On heating the mixture, however, this substance dissolved, and then the liquid darkened somewhat, after which benzoyloscine hydrochloride separated in almost quantitative yield, the mixture becoming solid. After allowing the reaction mixture to cool, it was crushed in a mortar and mixed with ether, the solid being collected, and washed with this solvent. On recrystallisation from alcohol, the benzoyloscine hydrochloride was obtained in tufts of colourless needles, which melted and evolved gas at 266°. This melting point is higher than that previously given for the salt in question, namely, 249—250° (*Beilstein's Handbuch, Ergänzungsband*, III, p. 619), and in order, therefore, to confirm the identity of the product, it was converted into the aurichloride. This salt crystallised in small tufts of yellow needles and melted at 183—184°:

0·0864 gave 0·0284 Au. Au = 32·9.

$C_{15}H_{17}O_3N,HAuCl_4$ requires Au = 33·0 per cent.

Benzoyloscine nitrate, prepared from the above-described hydrochloride, was very sparingly soluble in water, from which it crystallised in long, colourless needles. It melted and violently evolved gas at 195°. The corresponding picrate crystallised well in flattened needles, and melted at 185° without decomposing.

Benzoyloscine (benzoylscopoline) has previously been prepared by the repeated evaporation of oscine benzoate with dilute hydrochloric acid (D.R.-P. 79864), but the above-described method is far more expeditious, and gives much better yields.

Benzoyloscine d-*Camphorsulphonate.*

The benzoyloscine obtained from the above-described hydrochloride was converted into its d-*camphorsulphonate.* This salt was dissolved in ethyl acetate containing a little alcohol, when, after some time, it separated in the form of a white powder. When examined under the microscope, this was seen to consist of minute, diamond-shaped crystals.

Benzoyloscine d-*camphorsulphonate* melted at 167—168°, but, although it was submitted to a prolonged fractional crystallisation, no evidence of resolution could be obtained:

0·1476 gave 0·3312 CO_2 and 0·0918 H_2O. C = 61·2; H = 6·9.

$C_{15}H_{17}O_3N,C_{10}H_{16}O_4S$ requires C = 61·1; H = 6·7 per cent.

0·4226, made up to 20 c.c. with water, gave α_D $+0°26'$ in a 2-dcm. tube, whence $[\alpha]_D$ $+10·3°$; $[M]_D$ $+50·6°$.

Resolution of Benzoyloscine d-*Bromocamphorsulphonate.*

The base was recovered from the previously-described *d*-camphorsulphonate, and neutralised with *d*-bromocamphorsulphonic acid. The salt so obtained crystallised fairly readily from water, but much more easily from a mixture of ethyl acetate and alcohol, forming colourless needles. After one recrystallisation, it had somewhat the appearance of a mixture, and melted at 234—239°, previously softening at 211°.

0·4068, made up to 20 c.c. with water, gave α_D $+2°2'$ in a 2-dcm. tube, whence $[\alpha]_D$ $+50·0°$; $[M]_D$ $+285·0°$.

Since *d*-bromocamphorsulphonic acid has $[M]_D$ $+271°$, it appeared that the benzoyloscine *d*-bromocamphorsulphonate was resolving.

It was again crystallised as before, when it seemed much less soluble, and melted at 238—244°.

0·3982, made up to 20 c.c. with water, gave α_D +2°4′ in a 2-dcm. tube, whence $[\alpha]_D$ +51·9°; $[M]_D$ +295·8°.

When recrystallised a third time, this salt yielded handsome, glistening needles, which melted sharply at 246—246·5°.

0·4092, made up to 20 c.c. with water, gave α_D +2°8′ in a 2-dcm. tube, whence $[\alpha]_D$ +52·1°; $[M]_D$ +297·0°.

This salt was evidently that of the dextrorotatory component of the racemic base, and since, as shown below, it yielded d-*oscine* on hydrolysis, it must be designated *benzoyl*-d-*oscine* d-*bromocamphorsulphonate*. Repeated crystallisation caused no further change in its melting point or rotatory power:

0·1437 gave 0·2767 CO_2 and 0·0800 H_2O. C=52·5; H=6·2.
$C_{15}H_{17}O_3N,C_{10}H_{15}O_4BrS$ requires C=52·6; H=5·7 per cent.

The molecular rotation of *benzoyl*-d-*oscine*, calculated from that of its *d*-bromocamphorsulphonate, is $[M]_D$ +26·0°, whence the basic ion has $[\alpha]_D$ +10·0°.

A small quantity of the above-described salt of benzoyl-*d*-oscine was treated with sodium carbonate, the base extracted with chloroform, and examined polarimetrically, when a reading of +0°25′ was obtained. It was evident, therefore, that the base could be obtained in the free state without suffering complete racemisation. A larger quantity of the salt was then decomposed, and the resulting base dissolved in 20 c.c. of 50 per cent. alcohol, when it had α_D +0°49′ in a 2-dcm. tube. Ten c.c. of the solution were subsequently found, on titration, to contain 0·1172 of base, whence $[\alpha]_D$ +3·5°; $[M]_D$ +9·75°. The fact that the value thus obtained for the rotation of benzoyl-*d*-oscine is lower than that previously calculated for the basic ion of benzoyl-*d*-oscine *d*-bromocamphorsulphonate ($[\alpha]_D$ +10·0°) may be due, in part, to racemisation, but it is probably largely owing to the fact that the free base is incompletely ionised when dissolved in 50 per cent. alcohol (compare Carr and Reynolds, this vol., p. 1328).

Attempts were made to isolate *benzoyl*-l-*oscine* d-*bromocamphorsulphonate*, but without success. A fraction of salt, melting at 219—227°, was, however, obtained, the basic ion of which had $[M]_D$ −4·7°.

Benzoyl-d-*oscine hydrochloride* was prepared from the corresponding *d*-bromocamphorsulphonate by double decomposition. It formed colourless needles, melting at 283—284°.

Benzoyl-d-*oscine nitrate* was similarly prepared. It was very sparingly soluble in water, and crystallised in irregular prisms, which decomposed violently at 200°, and differed considerably in appearance from the long needles of the corresponding salt of the inactive base.

Benzoyl-d-*oscine picrate* crystallised very readily in handsome, yellow needles, which melted at 211—212° without undergoing any decomposition, a behaviour very remarkable in a picrate melting at so high a temperature.

Benzoyl-d-*oscine aurichloride* crystallised much more readily than the corresponding salt of the inactive base. It formed yellow needles, melting at 189—190°.

Hydrolysis of Benzoyl-d-*oscine. Formation of* d-*Oscine.*

The quantity of base which was employed, as above described, for determining the rotatory power of benzoyl-*d*-oscine in 50 per cent. alcohol was hydrolysed by means of hydrochloric acid, steam being passed through the mixture for the removal of the benzoic acid formed. To ensure that this was thoroughly accomplished, the operation was continued for three days. The liquid was maintained at a practically constant volume, and examined polarimetrically from time to time, when it was observed that the optical rotation increased appreciably as the hydrolysis proceeded. When the change was complete, the mixture was made alkaline, and the resulting *d*-oscine rapidly extracted with chloroform. The chloroformic liquids were then concentrated somewhat, and extracted with hydrochloric acid, after which the acid liquid, which measured 23 c.c., had α_D +1°35′ in a 2-dcm. tube, whence the specific rotation of *d*-oscine is calculated at $[\alpha]_D + 77 \cdot 7°$. This result must, however, be regarded as only approximate.

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CXCIII.—*Note on the Constitution of* α-*Elaterin.*

By CHARLES WATSON MOORE.

UNDER the title of "elaterin," the British and United States Pharmacopœias recognise a crystalline principle obtained from elaterium—a sediment from the juice of the fruit of *Ecballium Elaterium*, A. Richard.

It has been shown by Power and Moore (*Pharm. J.*, 1909, [iv], **29**, 501) that elaterin consists of a mixture of two crystalline substances of apparently identical percentage composition, but having optical rotations of opposite sign, and which those authors have designated as α- and β-elaterin (Trans., 1909, **95**, 1985). Of these two substances, only the dextrorotatory, β-elaterin, possesses physiological activity, the lævorotatory, α-elaterin, which is the principal constituent of the elaterin of commerce, being quite inert.

Berg (*Bull. Soc. chim.*, 1897, [iii], **17**, 85) has stated that elaterin does not exist as such in the fruit of *Ecballium Elaterium*, but that it is formed, after the expression of the juice, by the action of an enzyme on an amorphous glucoside. This view is not in agreement with the results obtained by Power and Moore (Trans., 1909, **95**, 1985), it having been definitely established by those authors that no glucoside of elaterin was present in the fruit of *Ecballium Elaterium*. Recently, Berg (*Bull. Soc. chim.*, 1910, [iv], **7**, 385), in support of his earlier view, has described the characters of the so-called "glucoside" of elaterin, and recorded an analysis of it. This "glucoside" is, however, an amorphous, indefinite product, evidently consisting of a mixture of substances, and any deductions made from the analysis of such material with respect to its composition have little or no value. The present author therefore, with the concurrence of Dr. F. B. Power, sees no reason to depart from the view previously expressed (*loc. cit.*), that elaterin is not present in the form of a glucoside in the fruit of *Ecballium Elaterium*.

It has quite recently been shown by Power and Moore (this vol., p. 99) that α-elaterin likewise occurs in the fruit of *Citrullus Colocynthis*, Schrader, and the material employed in the present investigation was obtained from this source.

During the last few years elaterin has been the subject of a considerable number of investigations, and, while the presence of certain groups in the molecule has been established, there is still divergence of opinion among the different investigators as to the empirical formula of the substance.

The formula adopted for elaterin by the Pharmacopœias, namely, $C_{20}H_{28}O_5$, is that put forward by Zwenger (*Annalen*, 1842, **43**, 460), but more recently Berg (*Bull. Soc. chim.*, 1905, [iii], **35**, 435), Hemmelmayr (*Ber.*, 1906, **39**, 3652), and Thoms (*Apoth. Zeit.*, 1906, **21**, 803) have suggested different empirical formulæ, namely, $C_{28}H_{38}O_7$, $C_{24}H_{34}O_6$, and $C_{22}H_{30}O_6$ respectively.

Of these formulæ, that indicated by Thoms (*loc. cit.*) is not in agreement with the analytical results obtained by all other investigators, while those of Zwenger, Berg, and Hemmelmayr require almost identical percentages of carbon and hydrogen, as follows:

$C_{20}H_{28}O_5$ (Zwenger) requires C = 68·9; H = 8·0 per cent.
$C_{28}H_{38}O_7$ (Berg) „ C = 69·1; H = 7·8 „
$C_{24}H_{34}O_6$ (Hemmelmayr) „ C = 68·9; H = 8·0 „
$C_{22}H_{30}O_6$ (Thoms) „ C = 67·7; H = 7·7 „

Owing to the slight solubility of elaterin in most solvents, molecular-weight determinations of this substance by means of the cryoscopic or the ebullioscopic methods are not trustworthy, and different results have been obtained by various investigators. Thus, Pollak (*Ber.*, 1906, **39**, 3380) obtained results in agreement with Berg's formula by means of the cryoscopic method, using phenol as solvent, whilst by the employment of the ebullioscopic method, using ethylene bromide as solvent, he obtained figures more in agreement with the formulæ of Zwenger and Thoms. Power and Moore (*Pharm. J.*, 1909, [iv], **29**, 501), on the other hand, have obtained results in agreement with the formula of Berg by means of the ebullioscopic method, using chloroform as solvent.

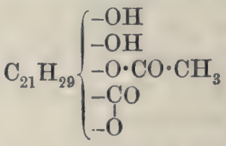
It is necessary, therefore, to have recourse to chemical methods to establish the molecular weight of this substance, but as all the hitherto described derivatives and decomposition products of elaterin are indefinite and amorphous, no satisfactory conclusions can be arrived at regarding their empirical formulæ.

It has been shown by Berg (*Bull. Soc. chim.*, 1905, [iii], **35**, 435) that when elaterin is treated for a short time with alcoholic sodium hydroxide, one molecule of acetic acid is split off, an amorphous, phenolic substance, "elateridin," being formed. Elaterin therefore appears to contain an acetyl group, and the estimation of the acetic acid formed by its hydrolysis affords evidence in support of Berg's formula.

Elaterin appears also to contain a lactone grouping, as by the prolonged action of boiling sodium hydroxide solution it is converted into "elateric acid," which, like "elateridin," is an amorphous product (Berg, *Bull. Soc. chim.*, 1905, [iii], **35**, 435; *Compt. rend.*, 1909, **148**, 1679). Thoms (*loc. cit.*) assumes the presence of two lactone groupings in elaterin, whilst Hemmelmayr (*loc. cit.*) explains the formation of "elateric acid" as being due to the oxidation of an aldehyde group. The latter explanation, however, does not appear to be tenable, for, although Hemmelmayr (*loc. cit.*) describes the preparation of a dihydrazone of elaterin (see also Berg, *Compt. rend.*, 1906, **143**, 1161), the present author has been unable to obtain any evidence as to the presence of a carbonyl group. The "hydrazone" described by Hemmelmayr is an amorphous, indefinite product, and there is no evidence that it is not a phenylhydrazide. Moreover, as such a compound would be obtained by the action of phenylhydrazine on a lactone grouping, this appears to be the most likely explanation of the nature of the product.

On heating elaterin with acetic anhydride, a diacetyl derivative is formed (Berg, *Bull. Soc. chim.*, 1905, [iii], **35**, 435; Hemmelmayr, *Ber.*, 1906, **39**, 3653). Elaterin must therefore contain two hydroxyl groups.

If it be assumed that the empirical formula put forward by Hemmelmayr is correct, α-elaterin might be written as follows:



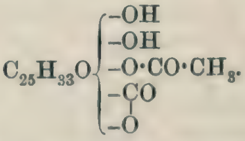
$$C_{21}H_{29}\begin{cases}-OH\\-OH\\-O\cdot CO\cdot CH_3\\-CO\\ \;\;|\\-O\end{cases}$$

On the other hand, if the empirical formula of Berg be adopted, there remains the state of combination of one oxygen atom to account for.

The present author has now been able to show that by the oxidation of "elateric acid" a definite, crystalline diketone is formed, which possesses the empirical formula, $C_{24}H_{30}O_5$, and may be designated *elaterone*.

As "elateric acid" is an indefinite, amorphous product, views as to its constitution, or even its empirical formula, based on analysis are of little or no value. It may, however, safely be assumed that it contains at least two carbon atoms less than elaterin, owing to the removal of the acetyl group from that substance in the course of its formation. As elaterone has now been shown to contain twenty-four carbon atoms, it follows that elaterin must contain at least twenty-six, and accordingly, to bring its formula into harmony with the analytical results, this must be written as $C_{28}H_{38}O_7$, in agreement with the formula of Berg.

In the present state of our knowledge, therefore, the formula of α-elaterin may be written as shown below, the manner of combination of one of the seven oxygen atoms being unknown:



$$C_{25}H_{33}O\begin{cases}-OH\\-OH\\-O\cdot CO\cdot CH_3.\\-CO\\ \;\;|\\-O\end{cases}$$

It is probable that the oxygen atom above referred to is present in the form of an ether linking, although, as has been shown by Pollak (*Ber.*, 1906, **39**, 3880), no methoxyl or ethoxyl group is present.

It has been shown by Thoms (*loc. cit.*) that elaterin is very probably a derivative of naphthalene, since by oxidising elaterin, and distilling the product with zinc dust, he obtained *a*-methylnaphthalene. The present author, however, by the distillation of elaterin itself with zinc dust, has obtained 1:4-dimethylnaphthalene.

EXPERIMENTAL.

The *a*-elaterin employed in the present investigation was obtained from Turkish colocynth, consisting of the dried, peeled fruit of *Citrullus Colocynthis*, Schrader, as described by Power and Moore (this vol., p. 99).

As already stated by those authors (*loc. cit.*), *a*-elaterin forms colourless, hexagonal prisms, melting and decomposing at 232°, and has $[\alpha]_D - 68.9°$ in chloroform solution (compare Berg, *Compt. rend.*, 1910, **150**, 981). On analysis, it gave results agreeing with those found by most other investigators for elaterin. (Found, C=68·9; H=8·1.)

A determination of the iodine value, by Hübl's method, gave the following result:

0·5010 absorbed 0·2673 iodine. Iodine value=53·3.

$C_{28}H_{38}O_7$, containing one double linking, requires iodine value=52·2.

a-Elaterin is insoluble in cold aqueous sodium or potassium hydroxide, but if it is suspended in a small quantity of alcohol, and potassium hydroxide (1 molecule) added to this mixture, the *a*-elaterin rapidly dissolves, and is not precipitated on pouring the alcoholic solution into twice its volume of water. On acidification, however, unchanged *a*-elaterin is precipitated. Hence it appears that *a*-elaterin possesses phenolic properties, and is capable of forming a potassium derivative soluble in alcohol. Attempts to isolate this potassium derivative were, however, unsuccessful, for on keeping the alcoholic solution, even in the cold, hydrolysis occurred with the formation of "elateridin." Attempts to prepare the corresponding methyl derivative by means of sodium ethoxide and methyl iodide were also unsuccessful.

With consideration of the statements of Berg and Hemmelmayr that elaterin contains a carbonyl group (*loc. cit.*), attempts were made to prepare a hydrazone and an oxime. An alcoholic solution of *a*-elaterin was boiled for about one hour with phenylhydrazine (1 molecule), but only resinous products resulted. Two experiments were accordingly made at the ordinary temperature. In both cases 1 gram of *a*-elaterin was dissolved in 100 c.c. of alcohol, and in one experiment 0·25 gram of phenylhydrazine was added to the solution, whilst in the second experiment, 0·5 gram of phenylhydrazine was used. The solutions were kept at the ordinary temperature for some hours, and were then diluted with water, when in both cases quantities of a yellow, resinous precipitate were produced. These precipitates were collected, and attempts were made to crystallise them from various solvents. In both cases small quantities of unchanged α-elaterin were recovered, but there was no indication of the formation of a definite hydrazone. Similar results were obtained on attempting to prepare an oxime. On boiling the alcoholic solution of α-elaterin with hydroxylamine, there was some decomposition, but when the experiment was conducted at the ordinary temperature (kept twenty-four hours), over 80 per cent. of the α-elaterin was recovered unchanged.

A quantity (10 grams) of α-elaterin was distilled, in small quantities at a time, with zinc dust in a current of hydrogen, when a small amount of an oily liquid, possessing a strong naphthalene-like odour, was formed. This was purified by distillation in a current of steam, but as the quantity of volatile substance so obtained was very small, it was converted into its picrate for identification. This crystallised from alcohol in small, orange-coloured needles, melting at 139°, and agreed in all respects with the picrate of 1:4-dimethylnaphthalene.

Alkaline Hydrolysis of α-Elaterin.

It has been shown by Berg (*loc. cit.*) that elaterin is hydrolysed by alkali hydroxides with formation of one molecule of acetic acid and either "elateridin" or "elateric acid," according to the extent of the hydrolysis. A determination of the acetic acid formed in this reaction was made as follows:

Twenty grams of α-elaterin were boiled for five hours with an excess of aqueous sodium hydroxide. The alkaline solution was then acidified with sulphuric acid, and the volatile acids removed by a current of steam. The acid distillate was found to consist of a mixture of acetic and formic acids.

The total volatile acids neutralised 1·791 grams NaOH, and the amount of formic acid was found to be equivalent to 0·151 gram NaOH. Hence the acetic acid was 2·460 grams = 12·3 per cent.:

$C_{26}H_{35}O_5\cdot O(CO\cdot CH_3)$ requires acetic acid = 12·3 per cent.

Oxidation of "Elateric Acid."

(1) *Formation of Elaterone*, $C_{24}H_{30}O_5$.

The "elateric acid" was prepared by the action of potassium hydroxide on α-elaterin, according to the method already described by Berg (*loc. cit.*). It forms a light brown, amorphous powder, soluble in sodium hydrogen carbonate, and appears to contain a carboxyl group. Neither the acid, nor any of its salts, has been obtained in a crystalline state. A determination of its specific rotatory power gave the following result:

0·3200, made up to 20 c.c. with ethyl acetate, gave α_D $+46'$ in a 2-dcm. tube, whence $[\alpha]_D$ $+23·9°$.

Ten grams of "elateric acid" were dissolved in 100 grams of glacial acetic acid, and 10 grams of chromic acid, dissolved in 12 grams of water, added, after which the solution was heated on a water-bath. A vigorous reaction occurred, and the liquid boiled spontaneously for some minutes. The mixture was subsequently heated for one hour, then poured into water, and, after the addition of sulphuric acid, it was extracted with chloroform. The chloroform extracts were shaken with aqueous sodium carbonate, which, however, only removed small quantities of resinous material. The chloroform solution was accordingly dried, and the solvent removed, when a quantity of a crystalline substance was obtained. This was recrystallised from boiling alcohol, when it formed long, colourless needles, melting at about 300°. The quantity so obtained amounted to 1·4 grams:

0·1135 gave 0·3000 CO_2 and 0·0805 H_2O. C = 72·1; H = 7·9.

After recrystallising from alcohol it was again analysed:

0·1390 gave 0·3680 CO_2 and 0·0974 H_2O. C = 72·2; H = 7·8.

$C_{24}H_{30}O_5$ requires C = 72·4; H = 7·5 per cent.

The molecular weight of the substance was determined by the cryoscopic method in benzene solution:

0·2616, in 22·34 c.c. benzene, gave $\Delta t = -0·154°$. M.W. = 380.

$C_{24}H_{30}O_5$ requires M.W. = 398.

As this substance does not agree in its properties with any compound of this formula which has hitherto been described, it is proposed to designate it *elaterone*, with consideration of the fact that it is a ketone (see below).

Elaterone is sparingly soluble in ether and alcohol, but readily so in chloroform and benzene. On heating, it sublimes in microscopic needles. It contains no hydroxyl group, being unaffected by prolonged boiling with acetic anhydride, and is not changed by boiling alcoholic potassium hydroxide. A determination of its specific rotatory power gave the following result:

0·2185, made up to 20 c.c. with chloroform, gave α_D $+2°38'$ in a 2-dcm. tube, whence $[\alpha]_D$ $+120·5°$.

Elateronemonophenylhydrazone.—Elaterone and phenylhydrazine readily interact in acetic acid solution, but if the mixture be heated, only resinous products result. When, however, the reaction is carried out in the cold, and only allowed to proceed for about fifteen minutes, a *monophenylhydrazone* is formed. This crystallises from dilute acetic acid in golden-yellow plates, melting and decomposing at 278°:

0·0988 gave 5·8 c.c. N at 24° and 746 mm. N = 6·4.

$C_{30}H_{36}O_4N_2$ requires N = 5·7 per cent.

Elateronedioxime.—Elaterone was boiled for some hours with an alcoholic solution of hydroxylamine. On concentrating the mixture, a dioxime separated in small, colourless plates, melting and decomposing at 295°:

0·2086 gave 11·0 c.c. N at 18° and 764 mm. N = 6·2.

$C_{24}H_{32}O_5N_2$ requires N = 6·5 per cent.

It is therefore evident that elaterone contains two carbonyl groups, both of which appear to be ketonic, as on boiling it with chromic acid solution, it is much more slowly oxidised than would be the case with an aldehyde.

A quantity (1·5 grams) of elaterone was boiled for one hour with chromic acid (1·5 grams: 6 atoms of oxygen) in acetic acid solution. At the end of this time, however, 0·5 gram of elaterone was recovered unchanged. No definite oxidation products of elaterone have as yet been obtained.

(2) *Formation of a Compound*, $C_{24}H_{32}O_4$.

If "elateric acid" be subjected to a somewhat milder oxidation than that described in connexion with the formation of elaterone, two crystalline products are formed, in about equal amounts.

A quantity (2·5 grams) of "elateric acid" was dissolved in glacial acetic acid (25 grams), and to the solution chromic acid (1·6 grams) dissolved in water (3 grams) was added. The solution was heated on a water-bath for one hour, and then worked up as in the previously described oxidation. In this case, however, a crystalline product was obtained, melting at 225—235°, which, after fractional crystallisation from alcohol, was separated into two substances, one of which melted at 295—300°, and was evidently elaterone, while the other formed glistening plates, melting at 230°. The quantity of the second substance was only 0·2 gram. Like elaterone, it was neutral towards alkalis, and did not react with acetic anhydride, but the quantity of material available was too small for full investigation:

0·1175 gave 0·3224 CO_2 and 0·0895 H_2O. C = 74·8; H = 8·5.

$C_{24}H_{32}O_4$ requires C = 75·0; H = 8·3 per cent.

It thus appears probable that this *substance* is an intermediate compound in the formation of elaterone, and that it yields the latter according to the following equation:

$$C_{24}H_{32}O_4 + 2O = C_{24}H_{30}O_5 + H_2O.$$

With the object of continuing this investigation, an attempt was made to obtain a further quantity of α-elaterin from a good specimen of commercial colocynth pulp, but only a very small quantity of the desired compound could be isolated. This result is somewhat remarkable, as Power and Moore (*loc. cit.*) had previously obtained over 1 per cent. of α-elaterin from Turkish colocynth pulp. It is therefore evident that the amount of α-elaterin contained in colocynth pulp may vary very greatly.

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CXCIV.—*The Molecular Complexity of Amides in Various Solvents. Part III. Amides in Aqueous Solution.*

By ANDREW NORMAN MELDRUM (Carnegie Research Fellow) and WILLIAM ERNEST STEPHEN TURNER.

IN order to bring the phenomenon of electrolytic dissociation in aqueous solution into connexion with fundamental ideas of electricity, J. J. Thomson advanced the hypothesis that water produces dissociation by reason of its high dielectric constant: "If the forces which hold the molecule together are electrical in their origin . . . these forces will be very much diminished when the molecule . . . is surrounded by a substance like water possessing a very large specific inductive capacity" (*Phil. Mag.*, 1893, [v], **36**, 313).

It is this hypothesis of Thomson which has originated the study of solvents in connexion with their dielectric constants, particularly of such as have a large constant. Notably, hydrocyanic acid, which has the constant 95, has been studied by Schlundt (*J. Physical Chem.*, 1901, **5**, 157), and formamide (constant >84) by Walden (*Zeitsch. physikal. Chem.*, 1905, **54**, 179, 181). The dielectric constant of water is 80.

Originally applied to the electrolytic dissociation of salts, Thomson's hypothesis was brought to bear by Nernst on the phenomenon of association in solution (*Zeitsch. physikal. Chem.*, 1894, **13**, 535). Association of a solute, on the supposition that this is caused by forces electrical in their origin, should be allowed by a solvent of low dielectric constant, and prevented by a solution of which the constant is high. This corollary of Thomson's proposition is denoted in this paper by the term the "Nernst-Thomson rule."

The authors have subjected the Nernst-Thomson rule to a very careful examination. They have already found good agreement with the rule for solutions of the amides—known to have a tendency to association—in five organic solvents, namely, ethyl alcohol, acetone, chloroform, ether, and benzene (Trans., 1908, **93**, 876; this vol., 1605). *n*-Butyramide, for instance, is highly associated in benzene, of which the dielectric constant is 2·3 at 18°, and normal in ethyl alcohol, of which the constant is 25·4 at 18·5°.

Water, however, presented notable exceptions to the rule. Certain amides, in solution in water, namely, benzamide, salicylamide, acetanilide, and dichloroacetamide, gave quite high molecular weights. These results were against all precedent and theory. No one had previously drawn attention to the fact that substances may be associated to as great an extent in water as in benzene. Further, the rule that the authors set out to test was found to hold good for five organic solvents, and ought to have proved specially sound in the case of water. Yet in this very case it broke down. The authors, in deciding to study the matter further, did so because the phenomenon of association in aqueous solution seemed to them of considerable importance in various directions.

EXPERIMENTAL.

The amides were the same as those used in part II of this series. The molecular weights were determined by the ebullioscopic method, using the same apparatus as before. The amount of solvent was ascertained both by weight and volume, and the authors have considered it advisable to give both sets of data. The reason for this is that the concentration necessary to produce a certain elevation of the boiling point of water is considerable, three to six times that for other solvents, and in consequence the divergence between weight and volume results is marked.

The solvent constants for water are (volume) 530, (weight) 510. In the following tables,*

V denotes volume of solution in c.c.
W denotes weight of solvent in grams.
Δ denotes elevation of boiling point (corrected).
N_w denotes the number of milligram-molecules of solute per 100 grams of solvent.
M.W.$_v$,, molecular weight determined by the volume method.
M.W.$_w$,, ,, ,, ,, ,, weight ,,

---

* These symbols were used in Part II., but the meaning of N_w was incorrectly stated there (*loc. cit.*, p. 1608).

Solvent—Water.

V.	*W.*	Δ.	N_w.	M.W.$_m$	M.W.$_w$
Propionamide (M.W. 73·1), 2·083 grams.					
20·6	17·83	0·705	159·8	75·9	84·5
24·6	21·26	0·596	134·0	75·4	83·8
28·8	25·18	0·507	113·2	75·5	83·2
36·7	33·50	0·382	85·1	78·7	83·0
42·0	37·98	0·336	75·2	78·1	83·3
Methylacetanilide * (M.W. 149), 2·681 grams.					
22·5	18·13	0·162	99·2	389	465
26·3	21·33	0·137	84·3	395	468
3·069 grams.					
22·1	17·70	0·141	116·3	523	627
2·037 grams.					
29·5	25·8	0·093	53·0	393	434
n-*Butyramide* (M.W. 87·1), 1·975 grams.					
31·2	27·82	0·346	81·5	97·0	104·6
37·8	34·07	0·289	66·6	95·7	102·3
43·1	39·32	0·261	57·7	93·0	98·1
49·7	45·57	0·227	49·8	92·8	97·4
iso*Butyramide* (M.W. 87·1), 2·060 grams.					
31·0	27·62	0·363	85·6	97·0	104·8
34·6	31·14	0·319	75·9	99·0	105·8
42·3	38·24	0·262	61·8	98·5	104·9
50·1	45·89	0·223	51·5	97·6	102·7
Valeramide (M.W. 101·1), 1·920 grams.					
24·3	20·86	0·345	91·0	122	136
28·8	25·24	0·296	75·2	119	131
35·1	31·74	0·248	59·8	117	124
42·1	38·14	0·209	49·8	115	123
iso*Butylacetamide* (M.W. 115·1), 2·209 grams.					
32·1	26·38	0·224	67·6	163	177
37·8	33·73	0·202	56·9	153	165
1·699 grams.					
25·2	22·36	0·218	66·0	164	178
30·6	27·17	0·183	54·3	161	174
Glycollamide (M.W. 75), 1·603 grams.					
26·0	23·94	0·447	89·3	73·2	76·4
30·3	28·13	0·395	76·0	70·9	73·6
36·4	34·13	0·300	62·6	77·7	79·8
45·7	42·94	0·236	49·8	78·7	80·7

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* This substance is volatile with steam, a source of error which we reduced to a minimum by carrying out several experiments, each giving one molecular-weight result. In addition, four molecular-weight determinations were made in series, with the object of observing the extent of distillation during the course of the work. The amount of anilide originally taken was 2·68 grams, and the amount remaining, after the 35 minutes which the series occupied, was found to be 1·94 grams.

Solvent—Water.

V.	*W.*	Δ.	N_w.	M.W.$_v$.	M.W.$_w$.
Lactamide (M.W. 89·1), 2·601 grams.					
22·8	19·39	0·717	147·5	84·3	95·4
26·4	22·92	0·612	124·7	85·2	94·6
30·9	27·44	0·517	105·2	86·3	94·4
36·7	32·94	0·431	86·8	87·1	93·4
Phenylacetamide (M.W. 135), 2·612 grams.					
25·0	21·69	0·297	89·2	186	207
29·2	25·40	0·269	76·2	176	195
41·1	37·07	0·210	53·4	160	171
2·101 grams.					
27·8	22·90	0·244	68·0	164	192
31·0	27·30	0·222	57·0	161	177
34·7	31·72	0·204	49·1	157	166
42·9	39·32	0·175	39·6	148	156
Formanilide (M.W. 121), 2·137 grams.					
26·6	23·65	0·238	74·6	179	194
32·0	29·00	0·211	60·8	168	178
1·548 grams.					
26·7	24·24	0·188	52·7	163	173
30·9	27·91	0·171	45·8	155	165
36·8	33·91	0·145	37·7	154	161
Glycollanilide (M.W. 151), 2·215 grams.					
30·5	27·34	0·210	53·6	183	197
36·3	33·24	0·177	44·1	183	192
42·9	39·14	0·159	37·4	172	181
52·3	48·26	0·134	30·4	167	175
Lactanilide (M.W. 165), 2·313 grams.					
23·7	20·95	0·230	66·9	224	245
27·5	24·05	0·213	58·2	209	230
31·2	27·59	0·188	50·8	209	227
35·1	31·57	0·171	44·4	204	218
42·0	38·02	0·149	36·8	196	208
Phenylcarbamide (M.W. 136), 1·174 grams.					
23·2	21·84	0·172	39·5	156	159
27·5	25·19	0·153	34·3	148	155
30·5	28·34	0·141	30·4	145	150
44·6	41·59	0·102	20·7	137	141

Experiment at the Freezing Point.

Urethane (M.W. 89·1).

W.	*w* (grams).	Δ.	M.W.
19·09	0·398	0·436	88·4
19·09	0·815	0·874	90·3
19·09	1·019	1·084	91·0

Examination of Results.

The results of the present investigation suggest that in water, despite its high dielectric constant, association is quite a frequent occurrence. To the four amides already found to be associated in water, the authors are able to add eleven out of the fourteen amides recently tested. (In what follows, the results of the previous investigation are shown by an asterisk.) Acetamide,* monochloroacetamide,* carbamide,* malonamide,* glycollamide, lactamide, and urethane are unassociated. Trichlorolactamide * is doubtful. Propionamide, *n*-butyramide, *iso*butyramide, valeramide, *iso*butylacetamide, glycollanilide, lactanilide, formanilide, acetanilide,* methylacetanilide, phenylacetamide, phenylcarbamide, benzamide,* salicylamide,* and dichloroacetamide * are associated.

This association presents a remarkable feature, which is best shown by putting the extent of association in water and in benzene side by side. As a means of comparison, the molecular weights and association factors are calculated at a concentration of 50 milligram-molecules per 100 c.c. of solvent, obtained from the weight data which, for solutions in benzene, were not given in full in the tables:

	In water.		In benzene.	
	M.W.	A. F.	M.W.	A. F.
Propionamide	83·0	1·14	148	2·03
n-Butyramide	97·6	1·12	172	1·98
*iso*Butyramide	102·8	1·18	169	1·94
Valeramide	123·0	1·22	184	1·82
*iso*Butylacetamide	173·0	1·50	206	1·79
Urethane	—	—	142	1·6
Glycollamide	80·5	1·07	—	—
Lactamide	92·0	1·03	—	—
Glycollanilide	196·0	1·30	340	2·25
Lactanilide	227·0	1·38	320	1·94
Formanilide	170·0	1·42	180	1·49
Acetanilide	194·0	1·44	—	—
Methylacetanilide	450·0	3·00	155	1·04
Phenylacetamide	170·0	1·26	—	—
Phenylcarbamide	170·0	1·25	—	—

A striking regularity is displayed in these data, namely, that the greater the tendency of a substance to molecular association in benzene, the less is its tendency in aqueous solution. As the figures in our first paper show, salicylamide is less associated in benzene than benzamide is, and in water the positions are reversed. Again, with the exception only of a slight deviation in the case of propionamide and *n*-butyramide in water, due possibly to slight experimental error, the tendency to molecular association in water rises from propionamide to *iso*butylacetamide, and falls in this order in benzene. Methylacetanilide, which has the normal molecular weight in benzene, shows apparent association of a very high order in water. Lactamide is not associated in water, and according to our rule should be strongly associated in benzene. Unfortunately, it is not soluble enough in benzene for the purpose, but there is good reason to think it is associated. One of us, in conjunction with Mr. E. W. Merry, has ascertained that it is strongly associated in the fused state. Phenylacetamide is moderately associated in water, in chloroform, and in the fused state. Urethane, which is associated in benzene, seemed to be associated in water also. It was suspected that the substance decomposes in water at 100°, and therefore the ebullioscopic was discarded in favour of the cryoscopic method. There was then no sign of association.

The Importance of the Phenomenon of Association in Water.

The authors hold that the unexpected association in aqueous solution, which they have demonstrated in the case of the amides, is not limited to these substances, but is of frequent occurrence. They have studied the amides, in the first place, as being, usually, soluble enough at 100°, and at the same time non-volatile. But certain other observations of association have been made. Jones and Getman, by the cryoscopic method, showed that acetic, oxalic, and succinic acids tend to form associated molecules in water (*Amer. Chem. J.*, 1904, **32**, 329).

The authors believe that this possibility of association in aqueous solutions has been left out of account in recent investigations to an injurious extent. Viscosity determinations as a means of detecting the formation of compounds between solute and solvent are in favour just now. From the determination of the viscosities of solutions in water of several organic acids, Tsakalotos (*Compt. rend.*, 1908, **146**, 1146) was led to think that formic acid produces no hydrate, whilst acetic, propionic, and *n*-butyric acids yield hydrates of the type $R\cdot CO_2H,H_2O$. Previously, however, Jones and Getman had concluded that there is no appreciable tendency on the part of acetic, oxalic, succinic, tartaric, and citric acids to form hydrates (*loc. cit.*, p. 338). Acetic acid certainly, and propionic and butyric probably, associate in water. Hence the authors would urge the necessity of considering that the molecules of the solute may associate with one another, as well as combine with water. A method of interpreting viscosity data which shall distinguish between these two possibilities is urgently needed.

In connexion with the "hydrate theory," the authors have made certain experiments of a similar character to those of Caldwell (*Proc. Roy. Soc.*, 1906, *A*, **78**, 272) and of H. E. Armstrong (*ibid.*, 1907, *A*, **79**, 576). These experiments consisted in observing the effect of several salts on the rate of inversion of sucrose by acids, and on the rate of hydrolysis of methyl acetate by hydrochloric acid. In place of a salt, that is, a dissociated substance, the authors have used methylacetanilide, which, as they had found, is strongly associated in water.

Experiments on the Inversion of Sucrose.

The effect of sodium chloride and of methylacetanilide on the inversion of sucrose was measured. Weight-normal solutions were used throughout. The temperature of experiment in each case was 40°.

Experiment 1.—One hundred c.c. of $N/4$-hydrochloric acid were mixed with 100 c.c. of 20 per cent. sucrose solution. Mean value of seven measurements of velocity constant, $K=7{\cdot}42\times10^{-3}$. Extremes, $7{\cdot}15$ and $7{\cdot}70\times10^{-3}$.

Experiment 2.—Solutions as before, with addition of 5 grams (0·085 mol.) of sodium chloride. Mean (5 measurements), $K=8{\cdot}65\times10^{-3}$. Extremes, $8{\cdot}60$ and $8{\cdot}71\times10^{-3}$.

Experiment 3.—Solutions as before, with addition of 5 grams (0·033 mol.) of methyl acetanilide. Mean (8 measurements), $K=8{\cdot}65\times10^{-3}$. Extremes, $8{\cdot}49$ and $8{\cdot}78\times10^{-3}$.

Equal amounts by weight of sodium chloride and methylacetanilide had apparently the same effect in accelerating the inversion of sucrose.

Experiments on the Hydrolysis of Ethyl Acetate.

Weight-normal solutions were again used. The temperature was 25°, which allowed only of a low concentration of methylacetanilide.

Experiment 1.—Two c.c. of ethyl acetate were mixed with 100 c.c. of $N/2$-hydrochloric acid. Mean of five measurements, $K=2{\cdot}63\times10^{-3}$. Extremes, $2{\cdot}52$ and $2{\cdot}71\times10^{-3}$.

Experiment 2.—Solution as before, with addition of 4 grams (0·068 mol.) of sodium chloride. Mean (6 measurements), $K\times3{\cdot}24\times10^{-3}$. Extremes, $3{\cdot}14$ and $3{\cdot}31\times10^{-3}$.

Experiment 3.—Solution as before, with addition of 2 grams (0·026 mol.) of methylacetanilide. Mean (6 measurements), $K=3{\cdot}05\times10^{-3}$. Extremes, $3{\cdot}01$ and $3{\cdot}08\times10^{-3}$.

The results show that the presence of methylacetanilide has an effect on these two chemical changes of the same kind as that due to sodium chloride. In the case of both hydrolysis and inversion the change is accelerated. Of the two substances, methylacetanilide has the greater effect, molecule for molecule. Supposing the withdrawal of water of hydration, by the added substance, to be the explanation of the accelerated inversion, or hydrolysis, as the case may be, it is obvious that methylacetanilide must be much more hydrated in solution than sodium chloride; for the same effect on the inversion of sucrose is produced by equal weights of the two substances, that is, by 1 molecule of methylacetanilide for 2·5 molecules of sodium chloride. If we assume that at the particular concentration employed, namely, 2½ per cent., the molecular hydration of sodium chloride is 14 (see, for example, Philip, Trans., 1907, **91**, 711), that of methylacetanilide must be about 35. Interpretation in this manner of the influence of methylacetanilide seems quite impossible. One cannot admit the possibility of combination between water and methylacetanilide to such an extent in the total absence of other evidence in this direction. There is, indeed, evidence to the contrary. Supposing methylacetanilide to combine with 35 molecules of water, we should expect it to give an abnormally high elevation of boiling point; for water is withdrawn from the rôle of solvent, and the solution is thereby concentrated. The reverse is the case: we find instead an abnormally low elevation. The hydrate theory, here at any rate, is entirely inapplicable.

At the present time, much work is being done on the problem of solution by the employment of what is regarded as an "indifferent" substance; that is, the substance and the solvent are supposed to be indifferent to one another. The method is to observe either the effect on the solubility of the indifferent substance, produced by the presence of another substance, or vice versa, the effect on the solubility of the other substance due to the presence of the indifferent substance (compare Usher, Trans., 1910, **97**, 66; Fox and Gauge, *loc. cit.*, 377; and Findlay and Creighton, *loc. cit.*, 559). It may be pointed out here that of the substances employed in these researches, quite a number, either in the liquid state or in suitable solvents, are known to be associated.

That substances which, for the purposes of investigation, were regarded as "indifferent," should have a tendency to association, is a state of things which was probably not intended. Hence it is possible that Usher's test of Jahn's hypothesis, namely, that the solubility of a gas in a dilute solution of a non-volatile, indifferent substance is the same, under the same conditions of temperature and pressure, as in the pure solvent, may not be valid (Usher, *loc. cit.*, 76). In the opinion of the authors, associated substances cannot be regarded as indifferent, and this opinion receives strong support from the experiments just detailed, in which methylacetanilide was employed. In these experiments, methylacetanilide, which is known to be associated, and sodium chloride, which is not supposed to be "indifferent," were found to produce effects of the same kind.

One line along which the working out of the problem suggests itself, by reason of the fact that the more nearly normal in organic solvents is the amide, the more strongly it appears to be associated in water, is that the molecular structure of water must be taken into account, in such a way as to admit that sometimes the structure may become more complex and sometimes simpler.

Here the authors would draw attention to the work of P. W. Robertson, on solution in phenol (Trans., 1903, **83**, 1904; 1904, **85**, 1425, 1617; 1905, **87**, 1574; 1906, **89**, 567), as having led him to results and conclusions in some respects similar to their own. He found that in phenol, itself an associated substance, the hydrocarbons and their halogen derivatives have high molecular weights. This abnormality the author believed "to be connected with the association of the phenol molecules, as the substituted phenols, which are less associated, tend [when used as solvents] to give normal results" (Trans., 1906, **89**, 570).

Within the last three years, H. E. Armstrong (*Proc. Roy. Soc.*, 1908, **81**, *A*, 80; 1909, **81**, *B*, 94) has formulated a theory of aqueous solution which involves the assumption that molecules of different degrees of complexity are present in liquid water, the various processes of solution involving the operation of these differently sized molecules.

The authors find themselves in agreement with the theory in so far as it appears to them necessary to take account of probable changes in the molecular complexity of water when solution occurs, differing with the nature of the solute. Moreover, since a substance which possesses a high molecular complexity has usually a high dielectric constant, these changes may well be accompanied by alterations in the dielectric constant of water, which cannot but react on the condition of the solute.

The authors desire to thank Mr. E. W. Merry, M.Sc., of the University of Sheffield, for carrying out the experiments on the inversion of sucrose and the hydrolysis of ethyl acetate.

The materials employed in this investigation were obtained by means of grants from the Government Grant Committee of the Royal Society and the Executive Committee of the Carnegie Trust for the Universities of Scotland.

THE UNIVERSITY,
MANCHESTER.

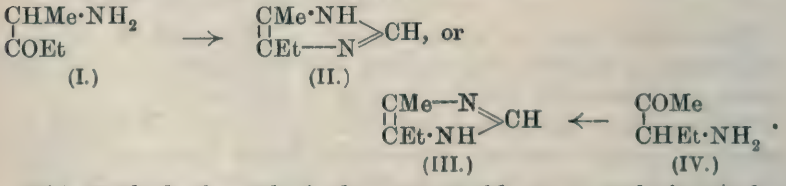
THE UNIVERSITY,
SHEFFIELD.

CXCV.—*The Tautomerism of Glyoxalines and the Constitution of Pilocarpine.*

By Frank Lee Pyman.

Since the suggestion of Pinner and Schwarz (*Ber.*, 1902, **35**, 2441), followed by the experimental proof adduced by Jowett (Trans., 1903, **83**, 438), that the glyoxaline radicle is contained in the alkaloid pilocarpine, and later the discovery by Pauly (*Zeitsch. physiol. Chem.*, 1904, **42**, 508) of this radicle in histidine, synthetic experiments with glyoxalines have attracted the attention of a number of chemists. Quite recently an added stimulus has been given to the work through the discovery by Barger and Dale (Proc., 1910, **26**, 128) that β-iminazolylethylamine, a compound which was recently synthesised by Windaus and Vogt (*Ber.*, 1907, **40**, 3691), is one of the active principles of ergot.

Some years ago Dr. Jowett (Jowett and Potter, Trans., 1903, **83**, 464; Jowett, Trans., 1905, **87**, 405), with a view to syntheses in this field, commenced a series of investigations, which will be referred to in detail later, and more recently, being unable to resume the work personally, requested the present author to continue it. The most important result of the present investigation is the proof that glyoxalines, containing a free imino-hydrogen atom, are tautomeric, a fact which previous research on the subject had already made probable. Thus, Jänecke (*Ber.*, 1899, **32**, 1098) prepared, by the oxidation of the mercaptan formed by the action of potassium thiocyanate on α-aminodiethyl ketone (I), the same methylethylglyoxaline (II or III) which Gabriel and Posner (*Ber.*, 1894, **27**, 1037) had previously obtained in a similar manner from α-aminopropyl methyl ketone (IV):



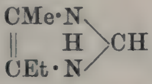
$$\begin{matrix}\mathrm{CHMe{\cdot}NH_2}\\ |\\ \mathrm{COEt}\end{matrix} \longrightarrow \begin{matrix}\mathrm{CMe{\cdot}NH}\\ \|\\ \mathrm{CEt{-\!-}N}\end{matrix}\!\!>\!\mathrm{CH},\ \text{or}$$

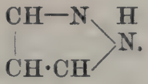
(I.) (II.)

$$\begin{matrix}\mathrm{CMe{-\!-}N}\\ \|\\ \mathrm{CEt{\cdot}NH}\end{matrix}\!\!>\!\mathrm{CH} \longleftarrow \begin{matrix}\mathrm{COMe}\\ |\\ \mathrm{CHEt{\cdot}NH_2}\end{matrix}.$$

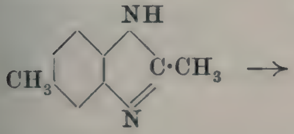
(III.) (IV.)

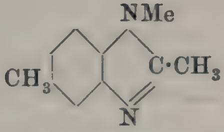
This method of synthesis does not enable any conclusion to be drawn as to which of the two isomerides, 5-methyl-4-ethylglyoxaline (II) and 4-methyl-5-ethylglyoxaline (III), is to be expected in each case, but it was inferred that a different one of the two would be expected in the two cases; the fact that the same methylethylglyoxaline was actually obtained in each case consequently showed either that this compound is tautomeric, or that one of the two forms (II) and (III) is the more stable. Jänecke thought the former view the more probable, and suggested that the imino-hydrogen atom vibrated between the nitrogen atoms in the same way as it does, according to Knorr (*Annalen*, 1894, **279**, 188), in the case of the pyrazoles:



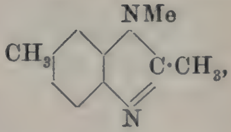


Several years later, Otto Fischer (*J. pr. Chem.*, 1906, [ii], **73**, 419; 1907, [ii], **75**, 88) prepared the 1 : 2 : 5- and 1 : 2 : 6-trimethylbenziminazoles by the action of methyl iodide on 2 : 5-dimethylbenziminazole:





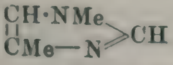
and



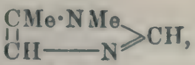
and thus showed that this compound is tautomeric.

In consequence of this result, and in order to demonstrate that the simple glyoxalines are also probably tautomeric, Gabriel (*Ber.*, 1908, **41**, 1926), who appears to have overlooked Jänecke's paper, brought forward another example of the formation from two different amino-ketones of a single 4 : 5-disubstituted glyoxaline, namely, phenylmethylglyoxaline. On the other hand, neither Jowett and Potter (*loc. cit.*) in the methylation of 4(or 5)-methylglyoxaline, nor Pinner (*Ber.*, 1905, **38**, 1535) in the ethylation of 4(or 5)-phenylglyoxaline, isolated two isomeric *N*-alkyl derivatives, and further, in more recent publications, both Pauly and Gundermann (*Ber.*, 1908, **41**, 4005) and Windaus (*Ber.*, 1909, **42**, 762) describe experiments with "α-*N*-dimethyliminazol"—presumably the methylation product of α-methylglyoxaline, that is, 4(or 5)-methylglyoxaline. The tautomerism of glyoxalines has therefore not hitherto been generally recognised.

A definite proof of the tautomerism of simple glyoxalines is now brought forward, for it has been found that 4(or 5)-methylglyoxaline yields, on methylation, a mixture of two isomeric *N*-methyl derivatives, 1 : 4- and 1 : 5-*dimethylglyoxaline* (V and VI) respectively:

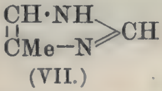


(V.)



(VI.)

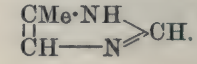
and therefore reacts according to both the formulæ (VII and VIIa):



$$\begin{array}{l}\mathrm{CH{\cdot}NH}\\ \parallel\\ \mathrm{CMe{-}N}\end{array}\!\!\gg\mathrm{CH}$$

(VII.)

and



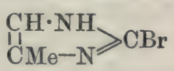
$$\begin{array}{l}\mathrm{CMe{\cdot}NH}\\ \parallel\\ \mathrm{CH{-\!-}N}\end{array}\!\!\gg\mathrm{CH.}$$

(VIIa.)

It may therefore be considered to react as a compound in which the hydrogen atom of the imino-group alternates in position between the two nitrogen atoms as suggested by Jänecke (*loc. cit.*) in the case of methylethylglyoxaline.

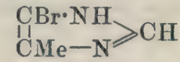
The formation of two isomeric *N*-methyl derivatives by the methylation of a glyoxaline has been confirmed by the methylation of the bromo-derivatives of 4(or 5)-methylglyoxaline.

The action on 4(or 5)-methylglyoxaline of bromine in a quantity sufficient to form a monobromo-substitution product has been tried at different temperatures, and it has been found that, even at −10°, the *monobromo*-derivative is accompanied by a considerable proportion of the *dibromo*-derivative, a corresponding quantity of 4(or 5)-methylglyoxaline being consequently unattacked. Only one monobromo-derivative has been isolated, and there is at present no evidence to show whether the substituent bromine atom occupies the 2- or the 4(or 5)-position. This compound is tautomeric, and reacts either as 2-bromo-4-methylglyoxaline (VIII) and 2-bromo-5-methylglyoxaline (VIIIa) or as 5-bromo-4-methylglyoxaline (IX) and 4-bromo-5-methylglyoxaline (IXa):



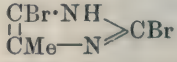
$$\begin{array}{l}\mathrm{CH{\cdot}NH}\\ \parallel\\ \mathrm{CMe{-}N}\end{array}\!\!\gg\mathrm{CBr}$$

(VIII.)



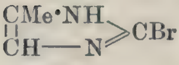
$$\begin{array}{l}\mathrm{CBr{\cdot}NH}\\ \parallel\\ \mathrm{CMe{-}N}\end{array}\!\!\gg\mathrm{CH}$$

(IX.)



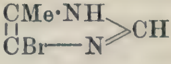
$$\begin{array}{l}\mathrm{CBr{\cdot}NH}\\ \parallel\\ \mathrm{CMe{-}N}\end{array}\!\!\gg\mathrm{CBr}$$

(X.)



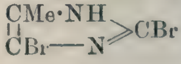
$$\begin{array}{l}\mathrm{CMe{\cdot}NH}\\ \parallel\\ \mathrm{CH{-\!-}N}\end{array}\!\!\gg\mathrm{CBr}$$

(VIIIa.)



$$\begin{array}{l}\mathrm{CMe{\cdot}NH}\\ \parallel\\ \mathrm{CBr{-\!-}N}\end{array}\!\!\gg\mathrm{CH}$$

(IXa.)



$$\begin{array}{l}\mathrm{CMe{\cdot}NH}\\ \parallel\\ \mathrm{CBr{-\!-}N}\end{array}\!\!\gg\mathrm{CBr}$$

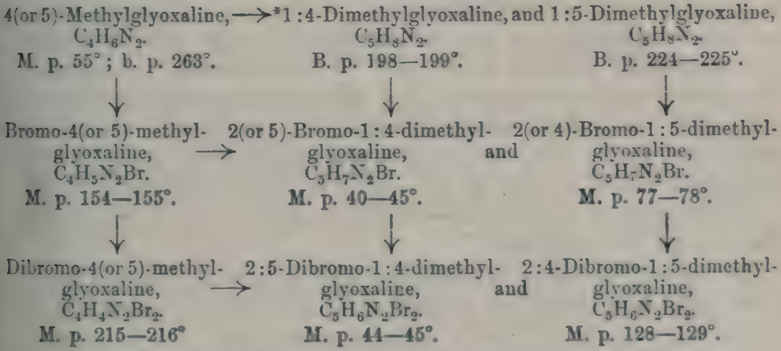
(Xa.)

The dibromo-derivative is also tautomeric, and reacts as 2:5-dibromo-4-methylglyoxaline (X) and 2:4-dibromo-5-methylglyoxaline (Xa).

Bromo-4(or 5)-methylglyoxaline yields, on methylation, a mixture of two isomeric *bromodimethylglyoxalines*, which melt at 40—45° and 77—78° respectively.

Dibromo-4(or 5)-methylglyoxaline similarly yields, on methylation, a mixture of two isomeric *dibromodimethylglyoxalines*, melting at 44—45° and 128—129°. The two dimethylglyoxalines obtained by the methylation of 4(or 5)-methylglyoxaline distil at 198—199° and 224—225°, and in order to determine which of the isomeric bromo- and dibromo-dimethylglyoxalines was derived from each dimethylglyoxaline, the latter bases were also brominated. Although the bromination of the two isomerides was carried out under precisely similar conditions, the results showed an interesting difference, the dimethylglyoxaline boiling at 198—199° yielding chiefly the corresponding monobromo-derivative which melts at 40—45°, and very little of the dibromodimethylglyoxaline which melts at 44—45°; whilst the dimethylglyoxaline boiling at 224—225° gave very little of the corresponding monobromodimethylglyoxaline melting at 77—78°, but chiefly the dibromodimethylglyoxaline melting at 128—129°.

The mutual relations between the isomeric dimethylglyoxalines and the various bromo-derivatives are shown by the following scheme:

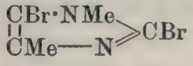

4(or 5)-Methylglyoxaline, $C_4H_6N_2$. M. p. 55°; b. p. 263°.
*1:4-Dimethylglyoxaline, $C_5H_8N_2$. B. p. 198—199°.
and
1:5-Dimethylglyoxaline, $C_5H_8N_2$. B. p. 224—225°.
Bromo-4(or 5)-methylglyoxaline, $C_4H_5N_2Br$. M. p. 154—155°.
2(or 5)-Bromo-1:4-dimethylglyoxaline, $C_5H_7N_2Br$. M. p. 40—45°.
and
2(or 4)-Bromo-1:5-dimethylglyoxaline, $C_5H_7N_2Br$. M. p. 77—78°.
Dibromo-4(or 5)-methylglyoxaline, $C_4H_4N_2Br_2$. M. p. 215—216°
2:5-Dibromo-1:4-dimethylglyoxaline, $C_5H_6N_2Br_2$. M. p. 44—45°.
and
2:4-Dibromo-1:5-dimethylglyoxaline, $C_5H_6N_2Br_2$. M. p. 128—129°.

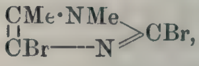
* The numbers are inserted in anticipation of the conclusions drawn later.

The question as to which series has the 1:4 and which the 1:5 arrangement of methyl groups is difficult to determine, and no direct evidence bearing on this point is brought forward at present. Fortunately, however, this matter can be settled with a high degree of probability by consideration of the relative affinities of the two dibromodimethylglyoxalines. These compounds are weak bases, and it has been found that the isomeride melting at 128—129° is very much more readily extracted by means of chloroform from its solution in 10 per cent. hydrochloric acid than the isomeride melting at 44—45°; the latter is therefore the stronger base.

Now, of the two nitrogen atoms in the glyoxaline molecule, the iminic nitrogen atom occupies a similar position to the nitrogen atom of pyrrole, and is almost devoid of basic properties. Glyoxalines behave as mono-acid bases, and the fact that their basicity is due to the nitrogen atom ·N⁚ has been clearly shown by Pinner and Schwarz (*loc. cit.*) by the formation of a mixture of monoalkylamines by the degradation of alkyl salts of *N*-substituted glyoxalines.

Consideration of the formulæ of the two isomeric dibromodimethylglyoxalines (XI and XII) shows that the basic 3-nitrogen atom:


(XI.)


(XII.)

is in both cases in close proximity to the strongly negative substituent bromine atom in the 2-position; the position of the other bromine atom relative to the 3-nitrogen atom is different in the two cases, and it seems reasonable to suppose that 2 : 5-dibromo-1 : 4-dimethylglyoxaline (XI), in which the second bromine atom is at a distance from the 3-nitrogen atom, will be a stronger base than 2 : 4-dibromo-1 : 5-dimethylglyoxaline (XII), in which these groups are close together. On the assumption that this view is correct, the compound melting at 44—45° is 2 : 5-dibromo-1 : 4-dimethylglyoxaline, and consequently the dimethylglyoxaline boiling at 198—199° is 1 : 4-dimethylglyoxaline, the compound melting at 128—129° is 2 : 4-dibromo-1 : 5-dimethylglyoxaline, and the dimethylglyoxaline boiling at 224—225° is 1 : 5-dimethylglyoxaline.

The bearing of these results on the constitution of *iso*pilocarpine has now to be discussed.

By the distillation of this alkaloid with soda-lime, Jowett (Trans., 1903, **83**, 438) obtained a number of glyoxaline derivatives, of which one was shown to be a dimethylglyoxaline. For the purpose of comparison, Jowett and Potter (Trans., 1903, **83**, 464) prepared by the methylation of 4(or 5)-methylglyoxaline an *N*-methyl derivative, which they regarded as a simple substance, either 1 : 4- or 1 : 5-dimethylglyoxaline. The aurichloride and platinichloride of this base, after suitable crystallisation, were shown to be identical with the aurichloride and platinichloride respectively of the dimethylglyoxaline obtained from *iso*pilocarpine; the picrate of the synthetic base, however, although having the same melting point—167°—as the picrate of the dimethylglyoxaline from *iso*pilocarpine, was not identical with the latter, since the mixture melted at 140—145°. These facts led Jowett to the conclusion that the dimethylglyoxalines derived from *iso*pilocarpine, and obtained by the methylation of 4(or 5)-methylglyoxaline respectively, were isomeric and not identical, and he also concluded that they were the 1 : 4- and 1 : 5-dimethylglyoxalines, but that there was no evidence to show which of the two was 1 : 4 and which 1 : 5.

The repetition of the methylation of 4(or 5)-methylglyoxaline on a larger scale, which has been made possible by Windaus and Knoop's discovery (*Ber.*, 1905, **38**, 1166) of a convenient method for the preparation of this compound, has shown that the product obtained is a mixture of the 1 : 4- and 1 : 5-isomerides. A comparison of the properties of the two isomerides and their salts with those of the dimethylglyoxaline from *iso*pilocarpine recorded by Jowett (*loc. cit.*) is tabulated below:

		1 : 4.	1 : 5.	From *iso*-pilocarpine.
Base	B. p.	198—199°	224—225°	210—215°
	Sp. gr.	0·997	1·021	—
	$n_D^{20°}$	1·49042	1·49963	—
Aurichloride	M. p.	137—138°	218—219°	214—215°
	Solubility in alcohol	easily	sparingly	—
Platinichloride	M. p.	233°	246°	238—239° *
	Solubility in water.	fairly easily	sparingly	—
Picrate	M. p.	167—168°	168—169°	167°
Hydrochloride	M. p.	168—169°	194—195°	—
Hydrogen oxalate.	M. p.	105—106°	133—134°	—

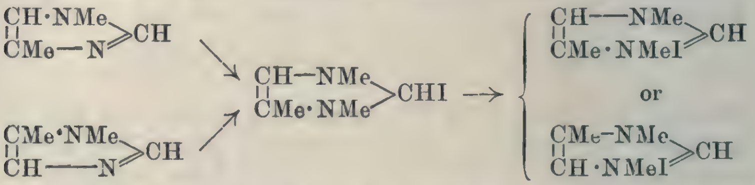
* When heated fairly quickly, this salt melted at 247°.

Through the kindness of Dr. Jowett, the author has had the opportunity of examining specimens of the picrate and platinichloride of the dimethylglyoxaline obtained from *iso*pilocarpine. The picrate melted at 167—168°, and mixtures of approximately equal amounts of this salt with (1) 1: 4-dimethylglyoxaline picrate at 140—145° and (2) 1: 5-dimethylglyoxaline picrate at 167—168°. The platinichloride, when slowly heated, decomposed at 238—239°, and mixtures with (1) 1: 4-dimethylglyoxaline platinichloride at 220° and (2) 1: 5-dimethylglyoxaline platinichloride at 239°; when fairly quickly heated, however, the platinichloride decomposed at 247°, and the mixture with 1: 5-dimethylglyoxaline platinichloride at 248°; the platinichloride of the dimethylglyoxaline from *iso*pilocarpine is sparingly soluble in water. Consideration of the table and the above facts shows that the dimethylglyoxaline from *iso*pilocarpine is identical with the isomeride of higher boiling point, which there is good reason to believe is 1: 5-dimethylglyoxaline.

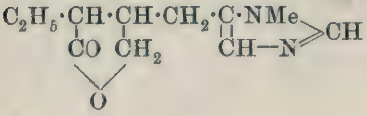
It is evident that Jowett and Potter's synthetic dimethylglyoxaline, which distilled mainly at 203° and had a specific gravity of 1·003, consisted chiefly of the 1: 4-isomeride of lower boiling point; the picrates of the two isomerides being of a similar solubility in water, they eventually obtained, after crystallisation of their picrate, the pure picrate of 1: 4-dimethylglyoxaline; recrystallisation of the aurichloride of their base from alcohol, however, gave them the pure 1 : 5-dimethylglyoxaline aurichloride, which is sparingly soluble in this solvent, whereas 1 : 4-dimethylglyoxaline aurichloride is easily soluble; similarly, recrystallisation of the platinichloride of their base from water yielded 1: 5-dimethylglyoxaline platinichloride, which is sparingly soluble in water, the

1 : 4-dimethylglyoxaline platinichloride remaining in the mother liquors.

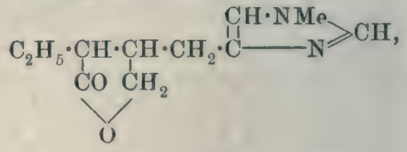
The methiodide prepared by Jowett and Potter from the synthetic dimethylglyoxaline may be obtained by the action of methyl iodide on either 1 : 4- or 1 : 5-dimethylglyoxaline. A similar case of the formation of only one methiodide from two isomeric benziminazoles has previously been described and explained by Otto Fischer (*loc. cit.*), on the assumption that methyl iodide is combined at the unsaturated linking, and that the compound produced then rearranges itself, forming the more stable of the two possible substituted ammonium iodides. This explanation is also applicable to the present case, and may be represented graphically as follows:



In conclusion, it may be pointed out that of the two alternative isomeric formulæ (I) and (II) put forward by Jowett (*loc. cit.*) for *iso*pilocarpine (compare also Pinner and Schwarz, *loc. cit.*), (I), which depicts the alkaloid as a 1 : 5-substituted glyoxaline, is supported by the fresh evidence now brought forward:



(I.)



(II.)

and since Jowett has shown (Trans., 1905, **87**, 794) that *iso*pilocarpine and pilocarpine are stereoisomerides, this evidence is equally applicable to the latter alkaloid.

EXPERIMENTAL.

Methylation of 4(*or* 5)-*Methylglyoxaline: Separation of the Isomeric* 1 : 4- *and* 1 : 5-*Dimethylglyoxalines.*

One hundred grams of 4(or 5)-methylglyoxaline were well shaken with 360 c.c. of 20 per cent. aqueous sodium hydroxide and 25 grams of methyl sulphate, the mixture being kept cold by running water; five further quantities of 120 c.c. of 20 per cent. aqueous sodium hydroxide and 25 grams of methyl sulphate were added successively with thorough shaking during the course of an hour. The liquor was then completely extracted with chloroform, and the extract dried with anhydrous potassium carbonate. After removal of the solvent, the resulting oil was distilled once under diminished pressure, and then fractionated three times under normal pressure, fractions being collected every 10° between 190° and 250°. As a considerable proportion of the oil distilled above 250°, it appeared that a part of the 4(or 5)-methylglyoxaline had escaped methylation, and the fractions boiling above 230°, and amounting to 31 grams, were consequently re-methylated. The product was fractionated, and the fractions suitably combined with those from the first methylation.

At this stage the products were as follows:

B. p...	190—200°	200—205°	205—210°	210—215°	215—220°	220—230°
Grams	**6·0**	**10·0**	**16·2**	**7·5**	**8·0**	**5·0**

After twelve fractional distillations of the above under normal pressure, the following fractions were obtained:

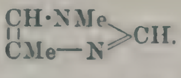
B. p...	195—200°	200—202°	202—205°	205—210°	210—215°	215—220°
Grams	17·0	5·0	3·8	3·6	2·3	4·5

B. p.	220—225°	above 225°.
Grams	8·4	3·8

The first fraction, b. p. 195—200°, distilled mainly at 198—199°, and represented nearly pure 1 : 4-dimethylglyoxaline. It was neutralised with dilute hydrochloric acid, and precipitated with picric acid, when 42 grams of the picrate, having the correct melting point, 167—168° (corr.), were obtained. After regeneration from the picrate, 1 : 4-dimethylglyoxaline distilled at 198—199° (corr.).

The fraction distilling at 220—225° was similarly converted into the picrate, and gave at first a quantity of pure 1 : 5-dimethylglyoxaline picrate, melting at 168—169° (corr.); the mother liquors and the picrates from adjacent fractions gave the same salt in a crude condition, and this was purified by crystallisation from water; altogether 19 grams of this salt were obtained in a pure state. After regeneration from the picrate, 1 : 5-dimethylglyoxaline distilled at 224—225° (corr.).

1 : 4-*Dimethylglyoxaline*,



$$\begin{matrix} \text{CH·NMe} \\ \| \\ \text{CMe—N} \end{matrix} \!\!>\!\text{CH.}$$

The base is a colourless, mobile, deliquescent liquid, having an odour somewhat similar to that of pyridine. It boils at 198—199° (corr.), and did not solidify after keeping for several hours in an ice-chest. It is miscible with water, alcohol, ether, and chloroform in all proportions, and a considerable amount of heat is developed when it is mixed with water or chloroform. It has a sp. gr. of 0·997 at 15·5°/15·5°, and a refractive index of 1·49042 at 20°:

0·1495 gave 0·3419 CO_2 and 0·1121 H_2O. C = 62·4; H = 8·3.
0·0538 „ 13·7 c.c. N_2 at 25° and 774 mm. N = 29·0.
$C_5H_8N_2$ requires C = 62·5; H = 8·4; N = 29·2 per cent.

The *hydrochloride* was obtained by neutralising the base with absolute alcoholic hydrochloric acid, and evaporating the salt to dryness in a vacuum desiccator over sulphuric acid. It separated in long, colourless, very deliquescent needles, which melted at 168—169° (corr.):

0·1408 gave 0·1537 AgCl. Cl = 27·0.
$C_5H_8N_2,HCl$ requires Cl = 26·7 per cent.

The *hydrogen oxalate* crystallises from absolute alcohol in prismatic needles, which, after drying in a vacuum, melt at 105—106° (corr.). This salt is readily soluble in water, but sparingly so in absolute alcohol:

0·1600, dried in a vacuum, gave 0·2637 CO_2 and 0·0841 H_2O. C = 44·9; H = 5·9.
$C_5H_8N_2,C_2H_2O_4$ requires C = 45·1; H = 5·4 per cent.

The *aurichloride* crystallises from alcohol in yellow, transparent, pointed prisms, which melt at 137—138° (corr.). It is sparingly soluble in water, readily so in cold alcohol, and very readily so in hot alcohol:

0·1725 gave 0·0869 CO_2 and 0·0371 H_2O. C = 13·7; H = 2·4.
0·2224 „ 0·1010 Au. Au = 45·4.
$C_5H_8N_2,HAuCl_4$ requires C = 13·8; H = 2·1; Au = 45·2 per cent.

The *platinichloride* crystallises from water in long, orange splinters, which decompose at 233° (corr.). It is fairly readily soluble in cold water, readily so in hot water, but almost insoluble in alcohol:

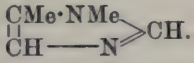
0·2015 gave 0·0647 Pt. Pt = 32·1.
$(C_5H_8N_2)_2,H_2PtCl_6$ requires Pt = 32·4 per cent.

The picrate and methiodide have already been described by Jowett and Potter (*loc. cit.*), who obtained them from the synthetic dimethylglyoxaline.

The picrate crystallises from water in beautiful, long, flat, yellow needles, which melt at 167—168° (corr.). It is sparingly soluble in cold water, but readily so in hot water.

The methiodide is produced with considerable evolution of heat when equimolecular proportions of the base and methyl iodide are mixed. It crystallises from absolute alcohol in long, stout, colourless splinters, which, when dried at 100°, melt to a viscous liquid at 160—163° (corr.). When the salt is mixed with an equal amount of the methiodide of 1:5-dimethylglyoxaline, its melting point is unchanged.

1 : 5-*Dimethylglyoxaline*,



$$\left.\begin{array}{l}\text{CMe·NMe}\\ \|\\ \text{CH——N}\end{array}\right>\text{CH.}$$

The base is a colourless, mobile, deliquescent liquid, having an odour somewhat similar to that of pyridine, but less intense than that of the 1 : 4-isomeride. It boils at 224—225° (corr.), and did not solidify after being kept for several hours in an ice-chest. It is miscible with water, alcohol, ether, and chloroform in all proportions, and a considerable amount of heat is developed when it is mixed with water or chloroform. It has a sp. gr. of 1·021 at 15·5°/15·5°, and a refractive index of 1·49963 at 20°:

0·1516 gave 0·3451 CO_2 and 0·1165 H_2O. C = 62·1; H = 8·6.
0·0743 „ 18·8 c.c. N_2 at 24° and 770 mm. N = 28·8.
$C_5H_8N_2$ requires C = 62·5; H = 8·4; N = 29·2 per cent.

The *hydrochloride*, prepared from the base and absolute alcoholic hydrochloric acid, separates in rectangular, oblong plates, melting at 194—195° (corr.), on evaporation of the solution in a vacuum over sulphuric acid. This salt is very deliquescent:

0·2134 gave 0·2313 AgCl. Cl = 26·8.
$C_5H_8N_2,HCl$ requires Cl = 26·7 per cent.

The *hydrogen oxalate* crystallised from absolute alcohol in stout, prismatic needles, which sintered at 132° and melted at 133—134° (corr.). This salt is readily soluble in water, but sparingly sc in absolute alcohol:

0·1515 gave 0·2523 CO_2 and 0·0764 H_2O. C = 45·4; H = 5·7.
$C_5H_8N_2,C_2H_2O_4$ requires C = 45·1; H = 5·4 per cent.

The aurichloride, platinichloride, and picrate of this base have previously been prepared by Jowett (Trans., 1903, **87**, 445) from the dimethylglyoxaline obtained by the distillation of *iso*pilocarpine with soda-lime; the aurichloride and platinichloride were also prepared from synthetic dimethylglyoxaline (Jowett and Potter, *loc. cit.*), and identified with the corresponding salts obtained from the alkaloid. It is therefore only necessary to describe them shortly.

The aurichloride crystallised from alcohol in yellow needles, which sintered and deepened in colour at 165° and decomposed at 218—219° (corr.). This salt is sparingly soluble in water or alcohol.

The platinichloride separated on adding platinic chloride to the aqueous solution of the hydrochloride in orange, rectangular leaflets, which began to darken at 239° and decomposed at 246° (corr.). When heated more rapidly, this salt decomposes at 249° (corr.). This salt is sparingly soluble in cold water, and almost insoluble in alcohol.

The picrate crystallised from water in short, yellow needles, which melted at 168—169° (corr.). It is sparingly soluble in cold water, but readily so in hot.

A mixture of approximately equal parts of this salt and of 1:4-dimethylglyoxaline picrate gradually sintered, softened considerably at 135°, and melted to a clear liquid at 140—145°.

The methiodide is formed with considerable evolution of heat when equimolecular proportions of 1:5-dimethylglyoxaline and methyl iodide are mixed, and, after crystallisation from absolute alcohol, forms long, stout, colourless splinters, which, when dried at 100°, melt at 160—163° (corr.); this salt is identical with 1:4-dimethylglyoxaline methiodide (p. 1822).

Bromination of 4(*or* 5)-*Methylglyoxaline.*

To a solution of 100 grams of 4(or 5)-methylglyoxaline in 600 c.c. of chloroform, 200 grams of bromine diluted to 300 c.c. with chloroform were added drop by drop with mechanical stirring, the temperature being maintained at −10° to −12°. The addition of the bromine occupied an hour, and the liquor was stirred for another half hour. It then formed a clear, pale brown solution, but when removed from the freezing mixture became turbid and began to separate into two layers, the upper one of chloroform, and the lower of brown oil, which soon began to crystallise. After keeping for a few hours, the crystals were separated from oil and chloroform by filtration, and washed with chloroform. The oil and chloroform were then separated, and the chloroform distilled, when a small further quantity of oil remained, which was added to the separated oil.

The crystals were heated for half an hour on the water-bath with a litre of water, when a part remained undissolved, and after keeping overnight, 27 grams of dibromo-4(or 5)-methylglyoxaline, melting at 210°, were collected (mother liquor M).

The oil was also heated for half an hour on the water-bath with a litre of water, but no crystals separated on keeping the solution; this was combined with the mother liquor M and fractionally precipitated with ammonia, when successively small fractions, melting at 205°, 175°, and 120—135°, and 30 grams melting at 145°, were obtained. On evaporating the ammoniacal liquor to low bulk, a further quantity of 35 grams of crystals, melting at 145°, separated; 33 grams of brown oil, which became partly crystalline, were obtained by extracting the mother liquor with chloroform, and a further 9 grams of brown oil were similarly extracted after the addition of aqueous sodium carbonate.

The various products were worked up as follows. The fractions which melted above 200° gave, on recrystallisation from ethyl acetate, pure dibromo-4(or 5)-methylglyoxaline, m. p. 215—216° (corr.); those melting at 145°, after recrystallisation from the same solvent, gave pure bromo-4(or 5)-methylglyoxaline, m. p. 154—155° (corr.). The mother liquors, after the removal of ethyl acetate and also those precipitated fractions which were obviously mixtures, were again separated by fractional dissolution in dilute hydrochloric acid and fractional precipitation with ammonia; in this way a further partial separation into crude dibromo-derivative melting at about 205—210°, crude bromo-derivative melting at about 135—145°, and intermediate fractions, was effected. On crystallisation of these fractions from ethyl acetate, further quantities of the pure compounds were obtained, and the residues were again subjected to the same cycle of operations.

The oil extracted by chloroform from the ammoniacal solution was extracted with water, which removed a quantity of 4(or 5)-methylglyoxaline, and, after fractional treatment with acid and alkali, gave further small quantities of the di- and mono-bromo-derivatives; the 9 grams of brown oil extracted by chloroform after the addition of sodium carbonate were nearly pure 4(or 5)-methylglyoxaline, and crystallised on keeping.

The total yield amounted to 36 grams of pure dibromo-4(or 5)-methylglyoxaline and 67 grams of pure bromo-4(or 5)-methylglyoxaline; there were also obtained 25 grams of viscid, dark brown, partly crystalline oil, which was not further purified, and about 18 grams of nearly pure unchanged 4(or 5)-methylglyoxaline.

The bromination has been carried out at various temperatures with the view of determining the best conditions for the production of the mono-bromo-derivative, with the following result:

One hundred grams of 4(or 5)-methylglyoxaline brominated at

5 to 10°	gave	52	grams of	dibromo-	and	58	grams of	monobromo-derivative
−4 to −7°	,,	46	,,	,,		62	,,	,, ,,
−10 to −12°	,,	36	,,	,,		67	,,	,, ,,

These figures refer, of course, to the quantities of pure compounds isolated; in each case there was also a dark brown, sticky residue, which could not readily be further purified, and some unchanged 4(or 5)-methylglyoxaline.

It should be mentioned here that when the bromination is carried out at 5° to 10° or −4° to −7°, the chloroform solution does not remain clear throughout, but gradually becomes turbid, and eventually crystals separate during the addition of bromine.

Bromo-4(*or* 5)-*methylglyoxaline* (VIII, VIIIa, IX or IXa, p. 1816).

This base crystallises from ethyl acetate in long, glistening, silky needles, which melt at 154—155° (corr.). It is sparingly soluble in cold water, fairly readily so in boiling water, and readily so in alcohol or ethyl acetate. It is soluble in dilute acids, dilute aqueous sodium hydroxide, or in a large excess of 10 per cent. aqueous ammonia, but not in 10 per cent. aqueous sodium carbonate:

0·1503 gave 0·1655 CO_2 and 0·0443 H_2O. $C=30·0$; $H=3·3$.
0·1004 ,, 14·7 c.c. N_2 at 16° and 768 mm. $N=17·3$.
0·1537 ,, 0·1809 AgBr. $Br=50·1$.
$C_4H_5N_2Br$ requires $C=29·8$; $H=3·1$; $N=17·4$; $Br=49·6$ per cent.

Aqueous solutions of this compound give with silver nitrate solution a white precipitate of the *silver* salt, which crystallises from boiling water in colourless, silky needles.

A solution of this base in dilute aqueous sodium hydroxide becomes deep orange in colour on the addition of aqueous sodium diazobenzene-*p*-sulphonate.

The *hydrogen oxalate* crystallises from water in colourless, prismatic needles, which begin to sinter at 205°, and decompose at 210° (corr.). It is anhydrous, and is very readily soluble in boiling water, but only moderately so in cold water:

0·1532 gave 0·1628 CO_2 and 0·0404 H_2O. $C=29·0$; $H=3·0$.
$C_4H_5N_2Br,C_2H_2O_4$ requires $C=28·7$; $H=2·8$ per cent.

Dibromo-4(*or* 5)-*methylglyoxaline* (X or Xa, p. 1816).

This compound crystallises from ethyl acetate in glistening, prismatic rods, which melt at 215—216° (corr.). It is almost insoluble in cold water, sparingly soluble in hot water, readily soluble in alcohol, and somewhat sparingly so in ethyl acetate. It is soluble in excess of dilute acids, and readily soluble in aqueous sodium hydroxide or 10 per cent. aqueous ammonia, but not in 10 per cent. aqueous sodium carbonate:

0·1489 gave 0·1111 CO_2 and 0·0261 H_2O. $C=20·3$; $H=2·0$.
0·1516 ,, 15·8 c.c. N_2 at 21° and 764 mm. $N=11·9$.
0·1490 ,, 0·2351 AgBr. $Br=67·1$.
$C_4H_4N_2Br_2$ requires $C=20·0$; $H=1·7$; $N=11·7$; $Br=66·7$ per cent.

Aqueous solutions of this compound give with silver nitrate solution a white precipitate of the *silver* salt.

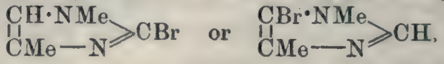
A solution of this base in dilute aqueous sodium hydroxide becomes deep orange in colour on the addition of aqueous sodium diazobenzene-*p*-sulphonate.

Methylation of Bromo-4(or 5)-methylglyoxaline.

Seventy grams of bromo-4(or 5)-methylglyoxaline were suspended in 300 c.c. of 10 per cent. aqueous sodium hydroxide, and well shaken while kept cold in running water with 14 grams of methyl sulphate, yielding a nearly clear solution. Quantities of 100 c.c. of 10 per cent. aqueous sodium hydroxide and 14 grams of methyl sulphate were added four times more, so that the total amounts used for the methylation were 700 c.c. of 10 per cent. aqueous sodium hydroxide and 70 grams of methyl sulphate. The addition of these quantities was carried through in one hour, and the mixture well shaken for ten minutes after the last addition.

The oil which had separated was then collected, and the aqueous liquor completely extracted with chloroform; the oil and chloroform were then mixed, dried with anhydrous potassium carbonate, and the solvent distilled. The chloroform residue amounted to 66 grams of brown oil, representing the mixed isomeric *N*-methyl derivatives. The mother liquor gave no more oil on re-methylation. The oil (66 grams) was combined with a similar product (44 grams) obtained by the methylation of another 50 grams of bromo-4(or 5)-methylglyoxaline, and kept overnight in a vacuum desiccator, when a quantity of 2(or 4)-bromo-1:5-dimethylglyoxaline separated in large, flat needles; this was collected, and amounted to 25 grams. The crystals and the oily liquor from which they separated were separately converted into the hydrogen oxalates, and crystallised from water; from the former a quantity of 2(or 4)-bromo-1:5-dimethylglyoxaline hydrogen oxalate was readily obtained in pure condition (m. p. 146—147°); from the latter, however, various crops of mixed hydrogen oxalates of the two isomerides, melting between about 85° and 95°, were obtained, and these were subjected to a prolonged fractional crystallisation from water. It was found that, on crystallising a mixture melting at about 90° from rather less than its own weight of water, fairly pure 2(or 5)-bromo-1:4-dimethylglyoxaline hydrogen oxalate, melting at 93—95°, would separate in large crystals on keeping overnight, and that the mother liquor, on scratching, would deposit a certain amount of crude 2(or 4)-bromo-1:5-dimethylglyoxaline hydrogen oxalate as a crystalline powder, melting at about 140°. Eventually, there were obtained altogether (from 110 grams of the mixed isomerides) 84 grams of pure 2(or 5)-bromo-1:4-dimethylglyoxaline hydrogen oxalate, melting at 95—97°, and 12 grams of the same salt in a fairly pure state, also 55 grams of pure 2(or 4)-bromo-1:5-dimethylglyoxaline hydrogen oxalate, melting at 146—147°, and 8 grams of the same salt in a moderately pure state, together with 10 grams of residues.

2(*or* 5)-*Bromo*-1 : 4-*dimethylglyoxaline*,



$$\begin{array}{l}\mathrm{CH{\cdot}NMe} \\ \| \\ \mathrm{CMe{-}N}\end{array}\!\!\!>\mathrm{CBr} \quad \text{or} \quad \begin{array}{l}\mathrm{CBr{\cdot}NMe} \\ \| \\ \mathrm{CMe{-}N}\end{array}\!\!\!>\mathrm{CH}.$$

This base was obtained, after regeneration from the pure hydrogen oxalate and extraction with ether, as an oil, which gradually solidified. It crystallises from anhydrous ether in beautiful, clear, colourless, quadrilateral plates, which melt at 40—45° (corr.), after sintering from about 35°.

The base is very deliquescent, readily taking up water, and forming an oil which is sparingly soluble in water. It is not more soluble in alkalis than in water, but is readily soluble in dilute acids. It is readily soluble in alcohol, ether, or chloroform:

0·2076 gave 0·2636 CO_2 and 0·0725 H_2O. $C=34·6$; $H=3·9$.
0·1769 „ 0·1908 AgBr. $Br=45·9$.
$C_5H_7N_2Br$ requires $C=34·3$; $H=4·0$; $Br=45·7$ per cent.

The *hydrochloride* crystallises from water in clear prisms, which, after drying at 100°, melt at 196—197° (corr.). It is very readily soluble in water or alcohol, but very sparingly so in acetone. Its aqueous solution reacts strongly acid:

0·1633 * gave 0·1681 CO_2 and 0·0567 H_2O. $C=28·1$; $H=3·9$.
0·2314 * „ 0·1583 AgCl. $Cl=16·9$.
$C_5H_7N_2Br,HCl$ requires $C=28·4$; $H=3·8$; $Cl=16·8$ per cent.

The *hydrogen oxalate* crystallises from water in large, irregular prisms, which melt at 95—97° (corr.), and contain one molecule of water of crystallisation. After drying, first in a vacuum and then at 100°, it melts at 133—135° (corr.). This salt is very readily soluble in hot water, and soluble in less than two and a-half times its weight of water at 25°:

0·1516 † gave 0·1659 CO_2 and 0·0533 H_2O. $C=29·8$; $H=3·9$.
0·1611 † „ 13·5 c.c. N_2 at 20° and 760 mm. $N=9·6$.
0·2093 † lost 0·0137 at 100°. $H_2O=6·5$.
$C_5H_7N_2Br,C_2H_2O_4,H_2O$ requires $C=29·7$; $H=3·9$; $N=9·9$; $H_2O=6·4$ per cent.

0·1440 * gave 0·1688 CO_2 and 0·0457 H_2O. $C=32·0$; $H=3·6$.
0·1834 * „ 0·1293 AgBr. $Br=30·0$.
$C_5H_7N_2Br,C_2H_2O_4$ requires $C=31·7$; $H=3·4$; $Br=30·2$ per cent.

The *picrate* crystallises from boiling water in long, flat, yellow needles, which melt at 223—224° (corr.), after sintering earlier. It is very sparingly soluble in water:

0·1534 gave 0·1835 CO_2 and 0·0362 H_2O. $C=32·6$; $H=2·6$.
$C_5H_7N_2Br,C_6H_3O_7N_3$ requires $C=32·7$; $H=2·5$ per cent.

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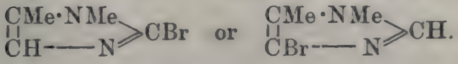
* Dried at 100°.

† Air-dried salt.

2(*or* 4)-*Bromo*-1 : 5-*dimethylglyoxaline*,



$\begin{array}{l}\mathrm{CMe{\cdot}NMe} \\ \| \\ \mathrm{CH{-}{-}{-}N}\end{array}\!\!>\mathrm{CBr}$ or $\begin{array}{l}\mathrm{CMe{\cdot}NMe} \\ \| \\ \mathrm{CBr{-}{-}{-}N}\end{array}\!\!>\mathrm{CH}.$

This base crystallises from ether in colourless, transparent splinters (or plates), which melt at 77—78° (corr.). When moistened with water, it becomes oily, and on the addition of a large quantity passes into solution. It is not more soluble in alkalis than in water, but dissolves readily in dilute acids. It is readily soluble in the usual organic solvents, with the exception of light petroleum:

0·1551 gave 0·1941 CO_2 and 0·0596 H_2O. C = 34·1; H = 4·3.
0·1517 ,, 0·1917 CO_2 ,, 0·0584 H_2O. C = 34·5; H = 4·3.
0·1683 ,, 22·3 c.c. N_2 at 13° and 770 mm. N = 15·9.
0·1493 ,, 0·1615 AgBr. Br = 46·0.
$C_5H_7N_2Br$ requires C = 34·3; H = 4·0; N = 16·0; Br = 45·7 per cent.

The *hydrochloride* crystallises from moist acetone in rectangular leaflets, which contain about half a molecular proportion of water of crystallisation, and melt at 93—94° (corr.). After drying at 100°, this salt melts at 172—174° (corr.). It is very readily soluble in water or alcohol, but sparingly so in acetone. Its aqueous solution reacts strongly acid:

0·2020 † lost 0·0106 in a vacuum over H_2SO_4. H_2O = 5·2.
$C_5H_7N_2Br,HCl,\frac{1}{2}H_2O$ requires H_2O = 4·1 per cent.

0·1569 * gave 0·1614 CO_2 and 0·0582 H_2O. C = 28·1; H = 4·2.
0·1912 * ,, 0·1296 AgCl. Cl = 16·8 per cent.
$C_5H_7N_2Br,HCl$ requires C = 28·4; H = 3·8; Cl = 16·8 per cent.

The *hydrogen oxalate* crystallises from water in magnificent, diamond-shaped, transparent plates, which melt at 146—147° (corr). This salt is anhydrous. It is very readily soluble in hot water, and soluble in four times its weight of cold water:

0·1489 gave 0·1743 CO_2 and 0·0494 H_2O. C = 31·9; H = 3·7.
0·1808 ,, 16·0 c.c. N_2 at 20° and 767 mm. N = 10·2.
$C_5H_7N_2Br,C_2H_2O_4$ requires C = 31·7; H = 3·4; N = 10·6 per cent.

The *picrate* crystallises from water in long, yellow needles, which melt at 198—199° (corr.), after sintering earlier. It is very sparingly soluble in water:

0·1518 gave 0·1830 CO_2 and 0·0346 H_2O. C = 32·9; H = 2·6.
$C_5H_7N_2Br,C_6H_3O_7N_3$ requires C = 32·7; H = 2·5 per cent.

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* Dried at 100°.

† Air-dried salt.

Methylation of Dibromo-4(or 5)-methylglyoxaline.

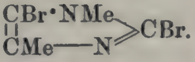
Fifty-five grams of dibromo-4(or 5)-methylglyoxaline were dissolved in 140 c.c. of 10 per cent. aqueous sodium hydroxide, and well shaken with 15 grams of methyl sulphate (half the calculated quantity), added in small quantities with thorough stirring and cooling under the tap. The solution began to deposit crystals shortly after the first addition of methyl sulphate; these were collected at the end of the methylation, and amounted to 24 grams. The mother liquor, after re-methylation with 90 c.c. of 10 per cent. aqueous sodium hydroxide and 15 grams of methyl sulphate, afforded another 20 grams of crystals, and the final mother liquor, when again methylated with the same quantities, gave a further 8 grams. The total yield of the mixed isomerides was therefore 52 grams, and each crop behaved in the same way on heating, sintering at 75°, and melting at 90—100. The mixture was separated by distillation with steam, when 2 : 5-dibromo-1 : 4-dimethylglyoxaline passed over very readily, and separated as a colourless oil, which solidified on cooling, and melted at 44—45°. As the distillation proceeded, a small quantity of colourless needles also separated in the receiver, and contaminated the oil, raising the melting point of the solidified oil somewhat; on redistilling with steam, however, the pure low melting isomeride again passed over first. The aqueous distillates still contain a considerable amount of this substance, but the bulk of it may be recovered by distilling these liquors, when it passes over quickly and largely separates from the first fraction; the remainder may be recovered by extraction with ether. The yield of 2 : 5-dibromo-1 : 4-dimethylglyoxaline amounted to 20·2 grams.

The residue of the steam distillation, consisting of 2 : 4-dibromo-1 : 5-dimethylglyoxaline, was purified by crystallisation from ethyl acetate, when it was obtained in beautiful, long, flat needles, which melted at 128—129° (corr.), and in quantity amounting to 20·1 grams.

The separation of the two isomerides may also be effected by crystallisation of the mixture from ethyl acetate; thus, 41 grams of the mixture (m. p. 90—100°), crystallised from 80 c.c. of ethyl acetate, gave at once 9·7 grams, melting at 125°, and, on concentrating, in various crops, 10·9 grams melting between 115° and 123°, then 1·5 grams melting at 90—100°; after removing the solvent from the mother liquor, an oil was obtained; this became solid, melted at 40—46°, and amounted to 17 grams.

By crystallisation of the fractions of high melting point from ethyl acetate, 18 grams of pure 2 : 4-dibromo-1 : 5-dimethylglyoxaline, and by distillation of the fractions of low melting point with steam, 13 grams of pure 2 : 5-dibromo-1 : 4-dimethylglyoxaline were obtained.

2 : 5-*Dibromo*-1 : 4-*dimethylglyoxaline*,



$$\left.\begin{array}{l}\mathrm{CBr{\cdot}NMe}\\ \|\\ \mathrm{CMe{-\!-}N}\end{array}\right>\mathrm{CBr}.$$

This compound crystallises from light petroleum in flat, prismatic rods, which sinter from 42° and melt at 44—45° (corr.).

It is very easily volatile with steam, sparingly soluble in water, and very readily soluble in the usual organic solvents. It is soluble in dilute acids, but not in alkalis:

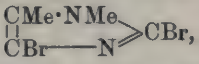
0·1516 gave 0·1325 CO_2 and 0·0322 H_2O. C = 23·9; H = 2·4.

0·1546 „ 14·3 c.c. N_2 at 16° and 763 mm. N = 10·8.

0·1034 „ 0·1538 AgBr. Br = 63·3.

$C_5H_6N_2Br_2$ requires C = 23·6; H = 2·4; N = 11·0; Br = 63·0 per cent.

2 : 4 - Dibromo - 1 : 5 - dimethylglyoxaline,



$$\left.\begin{array}{l}\mathrm{CMe{\cdot}NMe}\\ \|\\ \mathrm{CBr{-\!-}N}\end{array}\right>\mathrm{CBr},$$

has previously been described by Jowett and Potter (*loc. cit.*). It melts at 128—129° (corr.), and is soluble in 10 per cent. hydrochloric acid; it is only slightly volatile with steam.

The relative affinity of the two isomeric dibromodimethylglyoxalines has been roughly determined as follows.

0·5 Gram of each isomeride was separately dissolved in 10 c.c. of 10 per cent. aqueous hydrochloric acid, and each solution well shaken with 25 c.c. of chloroform. The chloroform extracts were filtered through a dry filter and evaporated to dryness. In the case of 2 : 5-dibromo-1 : 4-dimethylglyoxaline, the chloroform residue amounted to 0·05 gram, melting at 44—45° (corr.), that is, 10 per cent. of the quantity of base present; whilst in the case of 2 : 4-dibromo-1 : 5-dimethylglyoxaline, the chloroform residue amounted to 0·31 gram, melting at 128—129° (corr.), that is, 62 per cent. of the quantity of base present.

Bromination of 1 : 4-*Dimethylglyoxaline.*

Three grams of 1 : 4-dimethylglyoxaline were dissolved in 6 c.c. of chloroform, cooled with ice, and treated with a solution of 5 grams of bromine made up to 5 c.c. with chloroform added drop by drop in ten minutes with thorough stirring. On keeping, the red liquor remained clear; it was shaken with ammonia and water, dried with anhydrous potassium carbonate, and the solvent removed.

The residual oil was dissolved in just sufficient 10 per cent. aqueous hydrochloric acid, diluted, and distilled with steam; the first 30 c.c. of distillate carried over 0·1 gram of 2 : 5-dibromo-1 : 4-dimethylglyoxaline as an oil which solidified on keeping, and melted at 42—44°; a further 70 c.c. of clear distillate were collected, mixed with the 30 c.c. of distillate from which the solid had been separated, and redistilled, when a further 0·09 gram of the same dibromo-compound was obtained.

The acid liquor was then rendered alkaline, and again distilled with steam; the distillate, however, was quite bright even at the commencement, indicating that no considerable amount of the dibromo-compound was contained in the liquor. The liquor was then completely extracted with chloroform, giving 2·7 grams of brown oil; this was converted into the hydrogen oxalate and crystallised from water, when 3·0 grams of 2(or 5)-bromo-1 : 4-dimethylglyoxaline hydrogen oxalate, melting at 93—94°, separated; after recrystallisation from water, this salt melted at 95—97° (corr.).

Bromination of 1 : 5-*Dimethylglyoxaline.*

Three grams of 1 : 5-dimethylglyoxaline were brominated with 5 grams of bromine under the same conditions as its isomeride. The resulting orange-red liquor in this case deposited crystals on keeping, but these were not separated, the mixture being extracted several times with water to remove easily soluble hydrobromides.

The chloroform solution was then shaken with dilute ammonia, dried, and distilled, when 2·8 grams of 2 : 4-dibromo-1 : 5-dimethylglyoxaline were obtained as a buff, crystalline residue, melting at 127°; after recrystallisation from ethyl acetate, this compound melted at 128—129° (corr.).

The base regenerated from the aqueous extract of the chloroform solution amounted to 1·2 grams, and formed a pale brown oil; this was converted into the hydrogen oxalate, and twice recrystallised from water, when 0·3 grams of 2(or 4)-bromo-1 : 5-dimethylglyoxaline hydrogen oxalate, melting at 146—147° (corr.), were obtained.

The author wishes to take this opportunity of thanking Dr. Jowett, not only for his introduction to this subject, but also for his kind advice and interest throughout the investigation.

The Wellcome Chemical Works,
Dartford, Kent.

CXCVI.—*A Glucoside from Tephrosia purpurea.*

By George Clarke, jun., and Shrish Chandra Banerjee.

Tephrosia purpurea (Pers.)—nat. ord. *leguminosae*—a small, woody annual, is found all over India from the Himalayas to Ceylon, and in Assam, ascending to altitudes of 4000 feet.

Native works on Materia Medica describe the plant as deobstruent, diuretic, and useful in certain febrile attacks common in the East. When collected for medicinal purposes, the whole plant is gathered just before flowering, dried, and tied in bundles for sale (Watt, *Dictionary of the Economic Products of India*, Vol. VI, 1893, 15). The Pharmacographia Indica states that it contains resin, wax, and a yellow principle allied to quercetin or quercitrin. The latter has not been separated or examined. Owing to the similarity of *Tephrosia purpurea* and the cultivated varieties of the *Indigoferae*, it is known in the vernacular as "jungli nil"—wild blue or wild indigo—although it does not contain any indican or other substance yielding indigo.

Ten lbs. of sun-dried leaves, collected in the Cawnpore district at the end of August, were extracted with cold 95 per cent. alcohol for seven days. The alcoholic extract was drained off as completely as possible, and evaporated to a small bulk under atmospheric pressure. The green extract was poured into water, and washed with light petroleum until the green colour disappeared. The dark brown mother liquor deposited a copious crop of yellow crystals. The yield was about 2½ per cent. of the weight of dry leaves.

The crude substance was best purified by crystallisation from dilute acetic acid (1 : 3), and finally from dilute alcohol (1 : 1) or water. It crystallised in yellow needles, soluble in ethyl or methyl alcohols or acetic acid, very sparingly so in cold water, and insoluble in benzene, petroleum, or ether. It dissolved readily in dilute alkalis, giving a yellow solution, from which it could be precipitated by careful neutralisation with mineral acids. It began to sinter at 182°, and finally melted and decomposed at 184—186° (uncorr.).

The pure compound contained water of crystallisation, to which it clung very persistently under atmospheric pressure, and under these conditions required heating to 160° before the last traces of moisture could be expelled. It is easily obtained in an anhydrous state by heating in a vacuum at the boiling point of ethylene dibromide (131°).

The air-dried substance gave on analysis the following results:

0·698 lost 0·058 H_2O in a vacuum at 131°. $H_2O=8·30$.
0·222 „ 0·0182 H_2O „ 131°. $H_2O=8·19$.
0·9552 „ 0·0777 H_2O at 160°. $H_2O=8·13$.
1·6222 „ 0·1300 H_2O „ 160°. $H_2O=8·01$.
$C_{27}H_{30}O_{16},3H_2O$ requires $H_2O=8·13$ per cent.

The anhydrous substance is very hygroscopic, and regains water of crystallisation on exposure to air:

0·2650 gained 0·023. $H_2O=8·67$.
$C_{27}H_{30}O_{16}$ requires $H_2O=8·85$ per cent.

Separate fractions of the air-dried substance crystallised from water or dilute alcohol gave on analysis the following results:

0·2138 gave 0·3780 CO_2 and 0·1100 H_2O. C=48·22; H=5·71.
0·1810 „ 0·3210 CO_2 „ 0·0911 H_2O. C=48·36; H=5·59.
$C_{27}H_{30}O_{16},3H_2O$ requires C=48·79; H=5·42 per cent.

The anhydrous substance, dried in a vacuum at 131°, gave the following results:

0·2040 gave 0·396 CO_2 and 0·0956 H_2O. C=52·94; H=5·20.
0·2136 „ 0·4180 CO_2 „ 0·0974 H_2O. C=53·37; H=5·06.
$C_{27}H_{30}O_{16}$ requires C=53·11; H=4·91 per cent.

As the substance appeared to be a glucoside, it was examined in the following way. A solution of 20 grams in 1 litre of 2 per cent. sulphuric acid was digested at the boiling point for six hours. As the reaction proceeded, a yellow, crystalline precipitate separated out, and more was deposited on cooling. After being kept overnight, this substance was separated and examined. It was soluble in alkalis, giving a deep yellow solution, and yielded orange-coloured acid derivatives by treating in boiling acetic acid with concentrated hydrochloric, hydrobromic, hydriodic, or sulphuric acids.

The sulphate prepared in this way, washed with acetic acid and dried at 100° until constant in weight, was decomposed by water, and the sulphuric acid estimated:

0·343 gave 0·2004 $BaSO_4$. S=8·02.
1·135 „ 0·659 $BaSO_4$. S=7·97.
$C_{15}H_{10}O_7,H_2SO_4$ requires S=8·00 per cent.

The acetyl derivative, prepared from acetic anhydride in the usual manner, and crystallised from ethyl alcohol, melted at 190—191° (uncorr.). After being dried at 100°, it gave the following results on analysis:

0·2070 gave 0·4424 CO_2 and 0·0760 H_2O. C=58·28; H=4·07.
$C_{25}H_{20}O_{12}$ requires C=58·59; H=3·90 per cent.

The properties of this substance and the analysis of its derivatives left no doubt that it was quercetin.

The filtrate from which the quercetin had been separated was neutralised with barium carbonate, filtered, and evaporated to small bulk on the water-bath under atmospheric pressure. The solution examined in the polariscope was dextrorotatory. It was kept for some days in a partial vacuum over sulphuric acid, but gave no signs of crystallisation.

One gram of the dried syrup in 5 c.c. of water was mixed with 2 grams of phenylhydrazine hydrochloride and 4 grams of sodium acetate in 15 c.c. of water, and heated on the water-bath for three to four hours. Bright yellow crystals separated, which were washed with water and dried in the air. The melting point of the phenylosazone thus produced was 190—192° (uncorr.). When crystallised from dilute ethyl alcohol (1 : 1), it melted indefinitely at 190—195°, but when crystallised from pure ethyl alcohol the melting point was 206—207°, and this was not changed when the substance was mixed with *d*-phenylglucosazone.

Ten grams of the phenylosazone were prepared in the manner indicated above with specially purified phenylhydrazine hydrochloride. When fractionally crystallised from ethyl alcohol, it separated into two osazones. The sparingly soluble one melted at 206—207° (uncorr.), and the readily soluble one at 178—180° (uncorr.). The two substances were recrystallised three times each from ethyl alcohol. Their melting points remained unchanged. They differed in appearance, the fraction of higher melting point consisting of long, silky needles, characteristic of *d*-phenylglucosazone; the more readily soluble fraction crystallised in rosette-shaped clusters of small needles.

Pure phenylrhamnosazone prepared from pure rhamnose melted at 180—181° (uncorr.), and the melting point of a mixture of equal quantities of this substance and the readily soluble osazone from the *Tephrosia* glucoside sugars melted at 178—180°.

There is thus a very sharp separation into the two phenylosazones of rhamnose and dextrose resembling that described by W. Will in characterising the sugars of hesperidin and naringin (*Ber.*, 1887, **20**, 1186).

Somewhat prolonged heating is necessary in preparing the mixed osazones, as phenylrhamnosazone appears to be formed more slowly than the corresponding dextrose derivative.

d-Phenylglucosazone (the sparingly soluble osazone), m. p. 206—207°, when dried at 100° gave the following results on analysis:

0·151 gave 0·3328 CO_2 and 0·0861 H_2O. C = 60·10; H = 6·33.
0·2694 „ 0·593 CO_2 „ 0·1515 H_2O. C = 60·03; H = 6·24.
$C_{18}H_{22}O_4N_4$ requires C = 60·33; H = 6·14 per cent.

Phenylrhamnosazone (the readily soluble osazone), m. p. 178—180°, when dried at 100° gave on analysis the following results:

0·1971 gave 0·4537 CO_2 and 0·1182 H_2O. $C=62·77$; $H=6·66$.

$C_{18}H_{22}O_3N_4$ requires $C=63·16$; $H=6·43$ per cent.

A solution of the sugars from the hydrolysis of 20 grams of the pure glucoside from *Tephrosia purpurea*, from which quercetin and sulphuric acid had been separated in the manner described in the preceding experiments, was evaporated to 500 c.c., and cleared with a little washed animal charcoal. The colourless solution thus produced was treated with a few grams of ordinary brewer's yeast for four days at 35—40°. Active fermentation ensued, and a strong odour of alcohol was produced. After separating the yeast, the solution was evaporated to small bulk on the water-bath under atmospheric pressure, and finally dried in a vacuum over sulphuric acid. A few crystals were formed, but not enough to separate. The syrupy residue was warmed with 300—400 c.c. of ethyl alcohol, and a white, flocculent substance, which separated out on the addition of alcohol, was removed. The clear alcoholic solution was evaporated to about 50 c.c., and set aside to evaporate at room-temperature for a few days. About 2 grams of large, rhombic crystals, characteristic of rhamnose, were obtained, and a second crop of smaller crystals separated from the mother liquor.

The substance thus produced melted when carefully heated at 93—94° (uncorr.). The melting point of pure rhamnose under the same conditions was 93—94°, and a mixture of equal quantities of pure rhamnose and the rhamnose from the *Tephrosia* glucoside also melted at that temperature.

The rhamnose from the *Tephrosia* glucoside, dried in a vacuum over sulphuric acid, gave on analysis the following results:

0·1866 gave 0·2710 CO_2 and 0·1310 H_2O. $C=39·60$; $H=7·80$.

$C_6H_{14}O_6$ requires $C=39·56$; $H=7·69$ per cent.

The decomposition of the glucoside into quercetin, rhamnose, and glucose takes place in accordance with the following equation:

$$C_{27}H_{30}O_{16}+3H_2O=C_{15}H_{10}O_7+C_6H_{12}O_6+C_6H_{12}O_5,H_2O.$$

The decomposition was carried out quantitatively, the quercetin collected in a Gooch crucible, and dried at 160°:

0·544 air-dried glucoside gave 0·246 $C_{15}H_{10}O_7=45·22$.

$C_{27}H_{30}O_{16},3H_2O$ requires $C_{15}H_{10}O_7=45·48$ per cent.

0·639 anhydrous glucoside gave 0·315 $C_{15}H_{10}O_7=49·29$.

$C_{27}H_{30}O_{16}$ requires $C_{15}H_{10}O_7=49·50$ per cent.

Two substances have been described which closely resemble the *Tephrosia* glucoside, namely, osyritrin (*Osyris compressa*) and rutin, which is present in rue (*Ruta graveoleus*) and other plants. Whereas the former, $C_{27}H_{28}O_{16},3H_2O$, gives quercetin and dextrose (Perkin, Trans., 1897, **71**, 1134), the latter, originally considered by Schunck (Trans., 1888, **53**, 264) to yield only quercetin and rhamnose, has been found by Schmidt (*Arch. Pharm.*, 1908, **246**, 214) to have the formula $C_{27}H_{30}O_{16},3H_2O$, and to give, when hydrolysed, quercetin, rhamnose, and dextrose. Through the kindness of Mr. A. G. Perkin, a small sample of rutin was available for comparison, and as a result of experiment it was found that the *Tephrosia* glucoside is identical with this substance. On the other hand, it is interesting to note that Perkin (private communication) has found that osyritrin is identical with rutin [this vol., p. 1776].

The authors desire to express their thanks to the Managers of the Royal Institution of Great Britain for kindly placing the equipment of the Davy-Faraday Research Laboratory at their disposal for completing this investigation, which was begun in India; and to Mr. H. Martin-Leake, Economic Botanist to the United Provinces Government, for kindly identifying and growing the material used.

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INDIA.

CXCVII.—*Cupricitrates*.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

AN examination of the double carbonates of copper and sodium (Trans., 1909, **95**, 1409) led to the suggestion that in those of them wherein the copper is electronegative, it is present in the quadrivalent condition as :Cu:O, united directly with one † of the carbon atoms. The change of the copper atom into such a position from that which it usually occupies would be brought about by the conversion of a carboxyl group into two hydroxyls through the action of an alkaline hydroxide (β-compounds) or carbonate (α-com-

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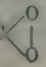
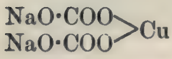
* Some time has elapsed since this paper was communicated to the Society (see Proc., 1910, **26**, 17), and portions of it have been so much elaborated by further work, that it has been considered advisable to reserve these for independent treatment.

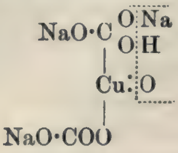
† It was originally represented as being united to both the carbon atoms; but this was unnecessary, and involved the somewhat unacceptable assumption of the group :C being present in the molecule.

pounds), the component atoms of which become added to those of the double salt, as indicated by the formulæ (1), (2) and (5):

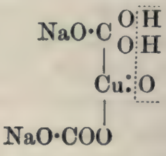


$$\begin{matrix}\mathrm{NaO{\cdot}COO} \\ \mathrm{NaO{\cdot}COO}\end{matrix}\!\!>\mathrm{Cu}$$

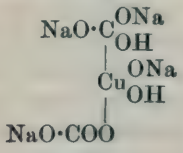
(1) Sodiocupric carbonate.



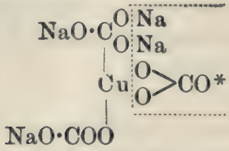
(2) *β*-Cupricarbonate.



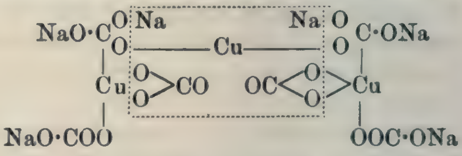
(3) *β*-Cupricarbonate.



(4) *γ*-Cupricarbonate.



(5) *α*-Cupricarbonate.



(6) *α*-Cupricarbonate.

The *γ*-cupricarbonate was not mentioned in the paper itself, but some evidence was given that the action of an alkali could be carried a step further than the formation of the *β*-compound (2), the copper, as well as the carbon, becoming hydroxylised, and being then in the "cuprite" condition; and it appears now, as was suggested in an addendum to the paper, that it was the *γ*-, and not the *β*-compound, which was present in the deep violet solution obtained, and described as containing the latter, since there was a large excess of sodium hydroxide present with it. This colour, as well as the property of combining with cellulose, appears to be characteristic of copper in the cuprite condition. Some facts have already been mentioned (*loc. cit.*, p. 1427) to show that a simple sodium cuprite may be obtained by the action of sodium hydroxide on copper oxide, and, also, that calcium cuprites exist.†

The double carbonate, or sodiocupric carbonate, is obtainable as a crystallised salt, but none of the cupricarbonates were isolated, and the evidence in favour of their existence has now been greatly strengthened by the isolation of numerous similar compounds in the case of citric acid. The two cases seem to be very strictly similar; double salts of analogous composition, exhibiting very similar properties, form the starting point in both series, and the final products of the action of alkalis are in both cases violet compounds, which oxidise dextrose in the cold, and combine with cellulose; whilst, in the case of citric acid, the existence of compounds containing potassium in the condition, both of hydroxide and of carbonate, has been established, by these being isolated in the crystalline condition, and several other similar salts, containing copper in the place of the alkali metal, have been prepared.

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* This group was originally represented as $:\mathrm{C}\!<\!{}^{\mathrm{O}}_{\mathrm{O}}\!>\!\mathrm{O}$, implying the direct union of oxygen atoms, which is now obviated.

† It would be preferable, in the writer's opinion, to adhere to the designation of cuprates, formerly applied, for salts derived from cupric oxide, rather than to reserve that term for the hypothetical derivatives of CuO_2. That the latter exist, and are red in colour, can scarcely be accepted, as maintained by Ramsay (Proc., 1910, **26**, 18), on the strength of Brauner and Kuzma having obtained a red compound which was "supposed to contain a tellurocupric acid" (*Ber.*, 1907, **40**, 3362).

In two particulars a modification of the views expressed as to the constitution of the cupricarbonates is suggested by the results obtained with the citrates. Firstly, that the α-compound is probably not formed by the combination of a molecule of the alkaline carbonate with a molecule of the double carbonate, as shown in (5), but by the combination of a molecule of sodiocupric carbonate with two molecules of the double carbonate, as shown in (6). Its empirical formula would, thus, be $3[Na_2Cu(CO_3)_2]$; and that it does consist of sodium and copper carbonates combined in equal molecular proportions is in accordance with the fact (*loc. cit.*, pp. 1418, 1425) that it is formed in maximum quantity when the reagents are present in such proportions. It may also be mentioned that what appears to be an analogous compound containing potassium has been isolated as a crystalline salt. Secondly, that the substance present in the solution from which the double salt is obtained is really a cupricarbonate, with its copper in the electronegative condition, which renders it possible to attribute the formula for sodiocupric carbonate (1) to the crystallised salt, instead of having to have recourse to the view that it is merely a molecular compound.

The cupricitrates described below are, with one exception, in which the substance is of a constitution different from that in other cases, characterised by certain general features. Unless the proportion of copper present in them is very large, they are all extremely soluble, dissolving in about a third of their weight of water at 8°. The solutions are of an intense blue colour, though of a dirtier tint than that of copper sulphate; they can be concentrated by heat, without decomposition, until a scum begins to form on the very viscid liquid; but crystallisation often does not begin for many days, and proceeds very gradually throughout several days more, until the whole becomes solidified, unless this is prevented by the addition of a little more water. Concentration of the liquid can be effected by adding alcohol. The crystals are microscopic in size, of a dead, somewhat light blue colour, and soft; on filtration from the liquid they form a putty-like mass, and can be purified by recrystallisation only with great difficulty. They gradually dry at 100° to an extremely hard mass, but most of them retain some water at this temperature, which they give up at 140—150°. The anhydrous compounds are blue and hygroscopic. On heating to a higher temperature they decompose quietly, this affording a convenient means of analysing them, the copper being determined gravimetrically as oxide, and the potassium volumetrically as carbonate.

Electronegative Copper.

The presence of a deep blue electronegative ion containing copper was proved in the case of the cupricarbonate by Wood and Jones (*Proc. Camb. Phil. Soc.*, 1907, **14**, 174), and in the case of the cupritartrate by Masson and Steele (Trans., 1899, **75**, 725): the apparatus devised by the latter—consisting of two tubes connected by a side-tube filled with agar agar in brine—has been used by the present writer for examining the cupricitrates, and it has been found that they, also, contain a dark blue, slow-moving, electronegative ion, although, during the electrolysis, a certain amount of a light blue, more rapidly-moving, electropositive ion makes its appearance, and results in a deposition of some copper on the negative plate. Copper in the electronegative condition does not, apparently, attack metallic iron, or react with ferrocyanide; but with the latter reagent, the electronegative copper appears gradually to be converted into electropositive, the red colour appearing in a space of time varying between a few seconds and many hours. None of the cupricitrates, except the one containing potassium in the alkaline condition, fail to react with ferrocyanide on long keeping; but that is not the case with certain other cupricompounds examined; potassium cuprisaccharate, for instance, although quite neutral, gives no trace of red with ferrocyanide, unless the solution has been previously boiled, but the boiled solution loses its power of reacting after the lapse of two days.

When no red ferrocyanide is formed—which is also the case if alkali hydroxide is present, either free or as an integral part of the salt—the liquid, if dilute, turns yellow, then green, and, after a long time, an orange precipitate, or ring at the surface of the liquid, forms, which is insoluble in acid, but dissolves in strong alkalis, being first converted by them into a blue substance. Excess of ferrocyanide is required for the formation of this compound.

The presence of free or combined carbonate does not interfere with the formation of the red copper ferrocyanide.

Compounds Obtained.

(1) *Potassiocupric Citrate*, $(C_6H_5O_7)_2CuK_4$.—When 100 grams of potassium citrate $(C_6H_5O_7K_3,H_2O)$ are dissolved in a small quantity of water on a water-bath with 8 grams of citric acid and 40 grams of copper citrate—which is a basic salt, $(C_6H_5O_7)_2Cu_3,CuO,2H_2O$—the liquid becomes converted into a mass of minute, irregular, hexagonal crystals, which, unlike the cupricitrates, are hard and gritty, and often adhere strongly to the dish. This substance continually makes its appearance when the reagents are taken in proportions other than those mentioned above, and also when no citric acid figures amongst them. It is of a very light blue colour, and although it dissolves to a large extent in water to form a deep blue solution—100 c.c. of a solution at 8°, containing 44 grams of the salt—it does so only very slowly, the result of which is that, when a stream of water is directed on to it on a filter, the moist blue substance becomes white wherever the water falls, and then gradually resumes its blue colour; a behaviour which renders it easily recognisable.

After drying over sulphuric acid or at 100°, various preparations of it gave as a mean:

Found: Cu, 10·56; K, 25·95; Ratio, 1 : 4·00.
Calculated: Cu, 10·63; K, 26·15; Ratio, 1 : 4.

This salt, consisting of two molecules of potassium citrate with two of the potassium atoms displaced by a copper atom, is analogous to the double carbonate of potassium and copper, and, as in the case of the citrate, the substance can hardly be represented as a molecular compound—the constitution of which would have to be $4C_6H_5O_7K_3 + 3[(C_6H_5O_7)_2Cu]$—the presumption is that the carbonate also is not a molecular compound. The nature of the two substances, and the similarity of their behaviour with water, gives further support to this view; as they are both light blue, crystalline substances, which in solution form very dark blue liquids.

That these liquids cannot be mere dissolutions of the crystallised substances is demonstrated in the case of the carbonate by the fact that the crystals will not redissolve in the mother liquor, and are decomposed by water. The liquids, it is suggested, contain a cupri-compound, formed by the addition of the elements of water to the double salt in a manner similar to that in which the alkaline β-cupri-compound is formed by the addition of the elements of KHO; the citrate would thus be

(2) A *β-cupricitrate*, $(C_6H_5O_7)_2K_4H_2CuO$, with a constitution similar to that represented by the structural formula (3), p. 1838.

The objection to such a view is that the copper in the dissolved substance appears to be in the electropositive condition, reacting completely with ferrocyanide at once, or very nearly so; this, however, has been proved to be due to the electronegative copper being in a very labile condition, for, on electrolysis, it is found that the copper, or the greater part of it, is really present in the electronegative ion, just as in the case of the other cupricitrates. It is also found that it has the same colour intensity and peculiarities as the copper in these other cupricitrates, this intensity being eighteen times that of the copper in copper sulphate (p. 1850). In the case of the cupricarbonate, the presence of electronegative copper was similarly demonstrated, even in those solutions which contained no excess of sodium carbonate, and the reaction of which with ferrocyanide had previously led to the conclusion that the copper in them must be electropositive (Trans., 1909, **95**, 1419).*

(3) *Potassium β-cupricitrate*, $(C_6H_5O_7)_2K_4HKCuO$, has not been isolated with certainty. On one occasion a small crop of microscopic, but comparatively large, crystals was obtained, which were strongly alkaline, and contained no carbonate; these were probably the compound in question, but they were not obtained in quantity sufficient for analysis. On mixing potassiocupric citrate with the requisite amount of potassium hydroxide, and concentrating by exposure over sodium hydroxide—an alkaline solution cannot be concentrated by heat, as copper oxide is thereby separated—a clear, deep blue, and almost solid syrup was obtained, which was still strongly alkaline. After some months, during which a little water had been added several times to it, and the liquid re-evaporated, it gradually became converted into a crystalline magma, which was quite neutral, and consisted probably of a mixture of some of the cupricitrates described below.

(4) *Potassium β-Cupricitrate*, $(C_6H_4O_7)_2K_6Cu,6H_2O$.—Luff obtained this salt by mixing potassium hydroxide, copper sulphate, potassium citrate and citric acid, and concentrating by shaking up with alcohol (*Zeitsch. Ges. Brauwesen*, 1898, **21**, 319). Jeffers, who, however, has not published his results, improved the method by substituting copper acetate for the copper sulphate. A still simpler procedure is to dissolve 40 grams of copper citrate in a hot, nearly saturated solution of 100 grams of potassium citrate, and to add to it, when the liquid has cooled to 40—50°, 20 grams of potassium

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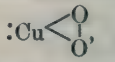
* It appears probable that some of the simple copper salts of organic acids may have, in solution, a constitution similar to that suggested for the double citrate in solution. It is remarkable that copper acetate does not act on iron. Salts of iron exhibit like peculiarities; thus, ferric citrate, when quite neutral, gives no reaction with ferrocyanide.

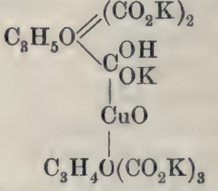
hydroxide in very strong solution. A copious crystallisation occurs, either at once, or on cooling, the crystals consisting of hexagonal tablets, generally very large, clear and regular, and of a fine violet-blue colour. They may be washed with a little water or alcohol, dried between blotting paper, and then by heating at 100° for a short time. The substance cannot be recrystallised, as in strong solution it soon decomposes, although in a dilute solution (containing about 0·1 per cent. of copper) it is quite stable, even on boiling. It is insoluble in a strong solution of potassium citrate. It loses a little water very slowly at 100°, and $6H_2O$ at 120—160°, forming a lavender-coloured mass, which redissolves in water, producing a solution identical in every respect with that obtained by dissolving the hydrated crystals. At 170° it becomes green, and on dissolution forms what is apparently a green solution, but this colour is due to the presence of minutely divided cuprous oxide, which eventually subsides, leaving a blue liquid. A similar decomposition occurs with other similar cupri-compounds, and has been misinterpreted in several cases as indicating the formation of some substance which is really green.

It has no action on metallic iron, and gives no red coloration with ferrocyanide, but the orange substance, mentioned above, is gradually formed if the ferrocyanide is in excess. It does not oxidise dextrose in the cold, but when boiled with it for a few minutes, cuprous oxide is precipitated, which redissolves slowly after cooling.

Many preparations of the salt were analysed, and all gave concordant results, the mean of which was:

Found: Cu, 8·09; K, 29·74; H_2O, 14·10; Ratio, 1 : 5·97 : 6·15.
Calculated: Cu, 8·13; K, 29·99; H_2O, 13·82; Ratio, 1 : 6 : 6.

This salt has been accepted as being potassium citrate with copper substituted for the hydrogen of the alcoholic hydroxyl; but such a constitution is quite inadmissible, for it is found that the potassium present in it is in two different conditions, one of the six atoms being present as alkaline hydroxide. The alkalinity was determined with sulphuric acid, using phenolphthalein as indicator, and evaporating the liquid repeatedly until the residue showed no further red colour on the addition of water: the mean result of many determinations gave 0·94K as being in the alkaline condition. The only formula that appears capable of expressing this fact is the following, in which the copper functions as in the case of the other cupricitrates, but also acts partly by displacing the hydrogen atom in one of the alcoholic hydroxyl groups, the formation of such a compound being explained by the addition of 2KOH to the molecule of potassio-cupric citrate, instead of 1KOH only, as in formula (2), p. 1838, which, resulting as it would in the formation of the unstable group  gives rise to rearrangement, with the liberation of the elements of water, and the formation of



$$+ 5H_2O.$$

An objection to this formula is that it represents the presence of only five molecules of water of crystallisation, so that, of the six lost on drying, one must be derived from the elements composing the body of the molecule. This is not very improbable, for on dehydration at a temperature a little above 100°, the water lost was found to be considerably less than $6H_2O$ (5·3 to $5·7H_2O$ in various cases), indicating that all the water present is not on the same footing. In any case, however, no argument based on the apparent water contents can counterbalance that depending on the alkalinity of part of the potassium in the salt.

In solution, this salt shows a colour intensity similar to that of the other cupricitrates, but its colour in the solid condition, as well as the size, hardness, and general appearance of the crystals, differentiates it entirely from the latter.

Bullnheimer and Seitz (*Ber.*, 1900, **33**, 817) obtained a salt which they represent as consisting of two molecules of Luff's salt combined with one molecule of a similar salt with K_2 in place of Cu; but no details respecting it were published, and the writer has not at present succeeded in preparing it.

(5) *Potassium a-Cupricitrate*; empirical formula,

$$[(C_6H_5O_7)_2CuK_4]_2,K_2Cu(CO_3)_2.$$

—When a concentrated solution of potassium carbonate is added to copper citrate dissolved in potassium citrate, some carbon dioxide is evolved, and, on evaporation, a mass of microscopic, acicular crystals is eventually obtained. They are alkaline in reaction, due to the presence of carbonate, not of hydroxide. The copper present is electronegative, as proved by electrolysis, and gives no reaction with ferrocyanide until after about one minute.

Four preparations, made with various proportions of reagents, gave the following values for the anhydrous substance:

	Found.		Calculated.	
	Per cent.	Ratio.	Per cent.	Ratio.
Cu	13·82	3·00	13·08	3
K (total)	28·34	10·00	26·82	10
K (alkaline)	5·51	1·94	5·36	2
CO_2	4·92	1·55	6·04	2

The water present in the specimens, after drying at 100°, was $2H_2O$ in one case, and about $6H_2O$ in the others.

The proportions of copper, total potassium, and alkaline potassium agree well with a formula similar to No. 6, p. 1838, representing a substance derived from two molecules of potassiocupric citrate united by one molecule of potassiocupric carbonate. The proportion of carbon dioxide is low, 1·55 instead of 2, due apparently to the fact that some of the compound to be next mentioned is always formed with the α-cupricitrate, and cannot be effectually separated from it by recrystallisation. In a preparation which evidently consisted of a mixture of these two substances, the proportion of alkaline potassium to CO_2 was found to be 1 : 1·07, which agrees well with the ratio 1 : 1 required on the view that $K_2Cu(CO_3)_2$ is present in the molecule.

In accordance with this view, it was found that potassiocupric carbonate dissolved easily and completely in a solution of potassiocupric citrate, even when dilute, although the double carbonate is entirely decomposed by water. The product thus obtained in the case of the citrate was not examined, but that obtained in the corresponding case of the tartrate was found to be a substance containing as part of its composition the elements of potassiocupric carbonate, as here indicated. In the case of the citrate, the dissolution of the double carbonate is always attended by the evolution of some carbon dioxide, so that some substance other than the α-cupricitrate must be formed at the same time, thus creating the difficulty mentioned above in obtaining the α-cupricitrate pure. With the tartrate there is no such evolution of gas, and no formation of other substances.

The addition of alkali hydroxide to the α-cupricitrate abstracts carbon dioxide from it, and precipitates a basic citrate (No. 10, p. 1848), which dissolves in excess of alkali, forming a deep violet solution. This action is precisely similar to that occurring in the case of the α-cupricarbonate.

The α-cupricitrate often makes its appearance in alkaline liquids which have been exposed to the air. From the liquids, also, which contained much potassium carbonate, were obtained on several occasions large, acicular crystals of $K_2CO_3,3H_2O$, which are remarkable in being, unlike the dihydrate and anhydrous salt, nonhygroscopic (Morel, *Bull. Soc. franç. Min.*, **15**, 7).

(6) *Tetrapotassio-cupric β-Cupricitrate*, $(C_6H_5O_7)_2K_4Cu,CuO$.—On the solidification of solutions of copper citrate in potassium citrate, there was repeatedly obtained a substance closely resembling the α-cupricitrate in general appearance, but very different in crystalline form: the crystals resembled straight hairs with truncated ends, the length of which was often fifty times greater than the breadth. They gradually grew together into rounded masses, projecting considerably above the liquid. Four samples on analysis after recrystallisation gave:

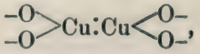
	Cu.	K.	H_2O at 100°.	Ratio.
Found:	16·63	22·85	5·22	2 : 4·36 : 2·22
Calculated:	17·82	21·92	5·06	2 : 4 : 2

These values are not very satisfactory, as there always seems to be some of the α-cupricitrate present, which cannot be eliminated by recrystallisation. A mixture of these two substances was recrystallised five times, whereby the relative proportion of the α-cupricitrate was greatly reduced, although there was still a considerable quantity of it left. Ascertaining the amount of this from determinations of the alkaline potassium and carbon dioxide present, and deducting the corresponding quantities of copper and potassium from the totals, the composition of the residue was given as:

Found: Cu, 19·48; K, 23·98; Ratio, 2 : 4·01.
Calculated: Cu, 18·76; K, 23·08; Ratio, 2 : 4.

The ratio here is satisfactory, and the discrepancy between the found and calculated percentages would be accounted for by a comparatively small error in the water determination.

The constitution of this compound may be represented as that of a β-cupricitrate similar to No. 3, p. 1838, with the hydrogen atoms of the two hydroxyls displaced by an atom of copper. It is probable that this copper is quadrivalent, and that two such molecules are joined together by means of it:



$$\begin{matrix}-O\\-O\end{matrix}>Cu\vdots Cu<\begin{matrix}O-\\O-\end{matrix},$$

for the whole of the copper in the compound appears to be electronegative, not acting on iron, and giving no colour with ferrocyanide until one or two minutes after it is added.

This substance may also be obtained by the decomposition of the following compound.

(7) and (8) *Dipotassio-dicupric β-Cupricitrate*,

$(C_6H_5O_7)_2K_2Cu_2,CuO$.

—When copper citrate is heated with a strong solution of potassio-cupric citrate, it dissolves, but in a few minutes the whole gradually solidifies to a light blue, crystalline mass. After a preliminary washing to remove soluble impurities, this is found to consist of (*a*) a small quantity of a dense, dark blue, scaly deposit, often adhering firmly to the dish, and only sufficiently soluble to give a faint reaction with ferrocyanide; and (*b*), a light blue solid, which, on washing with water for many days, yields continuously a solution containing 0·08 to 0·09 per cent. of copper. Analyses of both these solids, and of the solution obtained from (*b*), all gave the same ratio for the copper and potassium present:

	Ratio.				
	Cu	:	K.	:	H_2O.
Dense solid (*a*)	3	:	2·06	:	0·47
	3	:	2·04	:	—
Light solid (*b*)	3	:	2·08	:	—
Solution of (*b*) evaporated	3	:	2·13	:	0·92
	3	:	1·99	:	0·82

The mean results for (*a*) and (*b*) gave, for the anhydrous substance:

Found: Cu, 27·29; K, 11·53.
Calculated: Cu, 28·77; K, 11·80.

The proportion of water found in (*a*) indicates that the formula should be doubled, as suggested for the compound last described, (6), from which the present substance differs only in having an atom of copper substituted for two atoms of potassium. These latter may be different atoms in the case of the two compounds (*a*) and (*b*), thus accounting for the existence of two substances with the same formula. It acts, although very slowly, on iron, and gives some red colour at once with ferrocyanide; the greater part of the copper in it appears, however, to be electronegative, the full depth of colour being developed only on keeping. The colour-intensity of the copper in the solution is about eleven times that of copper in copper sulphate. In all these respects the characteristics of the substance tally with the formula suggested, which represents the presence of both electronegative and electropositive copper (see p. 1850).

The solution of (*b*) on evaporation leaves a residue which is decomposed by water, the cupricitrate, No. 6, $(C_6H_5O_7)_2K_4Cu,CuO$, passing into solution,* whilst ordinary basic copper citrate remains undissolved. This reaction indicates that the latter substance is really a

(9) *Copper cupricitrate*, $(C_6H_5O_7)_2Cu_3,CuO$, forming with the two last-described compounds a series of cupricitrates in which successive pairs of potassium atoms are displaced by copper atoms, with

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* This would probably be the best method for obtaining this compound in a state of purity.

progressive decrease in solubility. The peculiar lavender-blue colour of copper citrate indicates that it is probably not an ordinary basic salt.

(10) The *basic copper citrate*, $(C_6H_5O_7)_2Cu_3,4CuO$, precipitated by the action of alkali hydroxide on the α-cupricitrate (p. 1845), appears, on the other hand, to be a true basic salt. It is of a pure blue colour, and, unlike the cupricitrates, it loses all its water at 100°, and begins to decompose at 160°.

(11) A *Potassio-cupric β-Cupricitrate*, $(C_6H_5O_7)_3K_5Cu_2,2CuO$.—During the preparation of one of the cupricitrates, another substance was obtained in considerable quantity, consisting of very regular lenticular crystals, which were so small that they could not be resolved except under a high power of the microscope. Unlike any of the other compounds obtained, this substance is decomposed slowly by water, which accounts for the deficiency of potassium found in it on analysis, the sample having been slightly washed:

Found: Cu, 22·38 ; K, 15·55 ; Ratio, 4 : 4·64.
Calculated: Cu, 23·25 ; K, 18·64 ; Ratio, 4 : 5.

It contained about $3H_2O$ at 100°, which it lost at 160°, but this could not be determined satisfactorily, as it began to decompose at, or slightly above, this temperature. The substance is probably, as indicated, similar to No. 6, but derived from three, instead of two, citric nuclei; and the existence of such suggests the possibility of there being many more cupricitrates of complex character. By the action of water on it, a nearly insoluble residue was obtained, which was found to be the cupricitrate No. 8, whilst a blue solution was obtained containing copper and potassium in the ratio of 1 : 3, but whether in the form of a definite compound, or not, was not determined.

(12) *Potassium γ-Cupricitrate.*—Attempts to isolate the deep violet substance present in solution, when excess of alkali is added to any of the cupricitrates, failed. The liquid decomposes with the liberation of cupric oxide when concentrated, either by heat, or by exposure over sulphuric acid. Alcohol abstracts the excess of alkali from it, and Luff's salt is the only product obtained. The colour intensity of the copper in it is about eighty times that of copper in copper sulphate, but increases with the strength of the solution, and with the proportion of alkali added. As regards its colour, the precipitation of cuprous oxide from it by dextrose in the cold, and its combination with cellulose, it is closely similar to what has been described as the γ-cupricarbonate, as well as to other compounds (cupritartrates, etc.) obtained under like conditions.

(13) *Potassio-cupric Hydrogen Citrate*,

$$(C_6H_5O_7)_2K_4Cu,C_6H_5O_7KH_2,H_2O.$$

—On several occasions the residual liquid, after the crystallisation of some of the cupri-compounds, was of a light, greenish-blue colour, especially when citric acid had been taken as one of the reagents, and, on further evaporation, yielded a crop of fairly large, light green, hard crystals, with an acid reaction. They were stable in air, and began to decompose at 150°. On analysis, after drying at 100°, they gave values agreeing with the formula given above, which represents a molecular compound of potassio-cupric citrate with monopotassium citrate:

Found: Cu, 7·34; K, 23·29; Ratio, 1 : 5 04.
Calculated: Cu, 7·51: K, 23·10; Ratio, 1 : 5.

There is no reason for regarding this salt as a cupri-compound.

The Constitution and Colour of Cupri-compounds.

The isolation of so many cupricitrates agreeing in their properties, and, apparently, in their constitution, with the non-isolated sodium cupricarbonates, must lend considerable support to the views put forward as to the nature of the latter, especially when the salts isolated are found to include some in which the potassium is present in the condition of hydroxide and carbonate. A considerable amount of additional evidence has already been obtained, all tending in the same direction. Thus, several potassium cupricarbonates have been isolated in the crystalline condition, and these agree with the formulæ suggested for the sodium salts, and are, moreover, closely similar in their general characteristics to the cupricitrates here described. According to the views hitherto accepted, the cupricitrates would be represented, either as ordinary copper compounds with the metal displacing the carboxylic hydrogen, or as compounds with the metal displacing the hydrogen in the alcoholic group; according to the view now suggested, the copper is present in the molecule as $\dot{:}Cu\dot{:}O$, and the molecule contains, for each atom of copper present, the elements HHO over and above those present according to the ordinary views. It should be possible, therefore, to settle between the rival theories by determining the molecular weight of the compounds. The smallness of the differences to be measured, and the difficulty in obtaining the cupricitrates in a condition of sufficient purity, has rendered such determinations unsatisfactory in their case; but other similar compounds have now been obtained where such difficulties do not exist, and in every one of these instances, now numbering six, the molecular weight of the substance agrees closely with that required according to the present views.

In cases where a copper atom displaces the hydrogen of the two hydroxyl groups, as in No. 6, the properties of the substance seem to be conclusive against its being represented according to the hitherto accepted views; for according to these it would either be potassio-cupric citrate with CuO added on to it—that is, an ordinary basic salt—or potassio-cupric citrate, with copper displacing the hydrogen atoms of the alcoholic hydroxyl groups. Numerous compounds, however, have been obtained with copper in the "alcoholic" portion of the molecule, and these are all essentially different in their nature from this, or any of the other cupricitrates; whilst the extreme solubility of this compound must effectually negative the view that it can be a basic salt.

The accepted theory as to the constitution of cupri-salts affords no explanation of the formation of further products by the action of excess of alkali on them, such as must exist in the deep violet solutions thus obtained (γ-cupri-salts), or of the existence of compounds containing as part of their constitution the elements of alkali carbonates (α-cupri-salts).

Some interesting further evidence on the subject has been obtained from a study of the colour-intensity of these and other copper salts, to which a brief reference only can be made here. The molecular colour-intensity of copper in salts formed from strong acids has approximately the same value in all cases, and is independent of the concentration of the solution throughout the wide range over which comparison is possible. Taking this intensity as unity, that of copper salts derived from weak acids is much greater, reaching the value of 10 in some cases, and in every instance it diminishes as dilution increases, falling to 2 or 3 in most cases, and sometimes even to 1. With the cupri-compounds, however (Nos. 2, 4 and 6, for instance), the colour phenomena are very indifferent, indicating that the copper present must be in some peculiar condition, for the intensity is as high as 18, and remains constant down to extreme dilution. With the compound No. 7, p. 1846, the colour intensity, although still very high, is less than 18, and diminishes slightly on dilution, this being quite in accordance with the view that it is a cupri-compound, but one containing also some copper in the electropositive condition.

The view that copper may act as a tetrad is not new, although its behaviour as such receives very uncertain support from the existence of the oxide CuO_2. The extraordinary facility with which it enters into combination with carbon compounds would receive some explanation if its quadrivalent character is admitted, and its position in the periodic system, which is in any case anomalous, can afford no argument against such a view. That compounds in which copper is directly united to carbon should be explosive, because copper acetylide, the constitution of which is very uncertain, is such (see Ramsay, Proc., 1910, **26**, 19), is an argument which can scarcely carry much weight.

HARPENDEN.

CXCVIII.—*The Constitution of Basic Salts.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

No class of compounds has proved less attractive to chemists during the last half-century than basic salts; they have been accepted as necessary evils, cropping up where least required, and undeserving of any hypothesis to explain their constitution. They are, perhaps, regarded in a hazy way as being analogous to hydrated salts, although such a view can hardly be maintained, for the chief characteristics of hydrated salts are their solubility and powers of crystallising, whilst basic salts are mostly insoluble and amorphous compounds; in hydrated salts, moreover, the bond of union between the water and the salt is, in all probability, the oxygen atoms, whereas in basic salts it would appear to be the metallic atom. It is significant that no basic salts of univalent metals are known.

The want of interest evinced in these compounds is largely due to the fact that there seems to be no guiding principle governing in their formation, and that, in the large majority of cases, even their composition is a matter of considerable doubt. This may be said without any disparagement of the accuracy of the work on which we have to depend for our knowledge respecting them, for at the time when this work was done, ideas as to what constituted valid evidence of the individuality of a compound were very different from what they are now. Certainly our present neglect of basic salts is not justified by any inferiority in the part which they play in chemical changes; for in many manufactures, in the operations of agriculture, and in geological processes, they evidently play, or have played, a very prominent part, and we can hardly claim a satisfactory knowledge of simple salts until we know something of the numerous progeny of basic salts to which they give rise.

Some light appears to be thrown on the matter by a study of the basic sulphates of copper, in connexion with the facts established regarding the cupri-salts, for it is found that these basic sulphates gradually pass by successive steps from substances akin to ordinary copper sulphate to others wherein the copper is electronegative, ending with compounds which contain no sulphur at all, and which are, apparently, simple cuprites.

The series of substances formed by adding different proportions of lime-water to copper sulphate have already been described (Trans., 1907, **91**, 1989), and additional evidence respecting them was given in the Eleventh Report of the Woburn Experimental Fruit Farm. These results have been further elaborated recently, but a summary of them will be sufficient here.

Substances Precipitated from Copper Sulphate by Lime Water.

Down to (6) the liquids all contain 0·05 per cent. of copper.

Mols. CaO taken to 1 mol. $CuSO_4$. I.	Substance present. II.	Vol. of precipitate. III.	Percentage of copper in solution.		Change in dextrose in cold. VI.	Change in dextrose heated. VII.	Colour change on boiling. VIII.	Grams of iron dissolved IX.
			In water. IV.	In dextrose V.				
(2). 0·75	$4CuO,SO_3$ $(0\cdot06CaSO_4)$	4·1	0·0023	0·0021	nil	nil	nil ‡	0·0122
0·767	Mixture ...	4·7	0·0012	0·0015	nil	nil	nil ‡	—
0·784	,, ...	5·5	0·0005	0·0003	nil	nil	nil ‡	—
(3). 0·8	$5CuO,SO_3$ $(0\cdot25CaSO_4)$	6·5	0	0	nil	nil	nil ‡	0·0073
0·833	Mixture ...	8·3	0	0	nil	Dirty green[1]	Blackens[3]	—
0·867	,, ...	12·9	0	0	nil			—
(4). 0·9	$10CuO,SO_3$ $1\cdot3CaSO_4$	17·1	0	0	nil			0·0032
1·0	Mixture ...	17·3	0	0	Dirty green in 8 days	Dirty green and Cu_2O deposited[2]		—
1·1	,, ...	18·5	0	0	2 ,,			0·0014
1·15	,, ...	—	0	0	12 hours			—
(5). 1·2	$10CuO,SO_3$ $3CaO,CaSO_4$	16·3	0	0	1 hour		nil	nil
1·25	,, ,,	15·6	0	some *	Cu_2O deposited in 24 hours	Cu_2O deposited	nil	—
1·30	,, ,,	15·8	0	some *	3½ ,,		nil	—
1·35	,, ,,	13·4	0	some *	2½ ,,		nil	—
2·0	,, ,,	13·9	0	0·021	1 hour		nil	—
5a). 3·0	Mixture ..	7·7	0	0·032	1 ,,		Turns violet[4]	—
3·5	,, ...	—	0	—	½ ,,			—
4·0	,, ...	—	0	—	—			—
4·5	,, ...	—	0	0·050 †	—			—
(6). 25	$(CuO,2CaO)$	—	0	—	—	—		—
(7). 50	$CuO,3CaO$	—	0	—	—	—		—
100	,, ,,	—	0	—	—	—		—
150	,, ,,	—	0	—	—	—	nil	—

* Not determined.

† That is, all the copper dissolved.

‡ If freshly precipitated, these become greener and denser.

[1] Increasing in amount with increase of basicity.

[2] The amount of green decreasing, and that of deposited oxide increasing, with increase of basicity.

[3] The blackening increasing to a maximum at No. 4 and then decreasing.

[4] The least and most basic precipitate exhibiting a partial change only.

The members are numbered (2) to (7) in the above abbreviated table, and to these must be added two other basic sulphates obtained by other means. The first four contain some loosely combined calcium sulphate, but the amount is so inconsiderable in the case of the first two members, that its presence may be accidental. The proportions of CuO:CaO in Nos. 6 and 7 are uncertain; CuO,3CaO seems to be constant in composition throughout a wide range of proportions of lime-water added, but the existence of CuO,2CaO is doubtful; all that is certain is that some compound of the two oxides with less calcium than CuO,3CaO must exist, as the precipitate becomes destitute of sulphate before it attains the composition of CuO,3CaO. All the liquids after passing No. 4 are alkaline.

Columns III to IX contain details as to the behaviour of the various precipitates obtained by adding increasing amounts of lime-water to the same weight of copper sulphate, the total volume of the mixture being the same in all cases.

When first formed, whatever be the proportions taken, the precipitate is the same in appearance, being bulky, and of a full blue colour; but this soon changes to a light blue in the case of the the two lowest sulphates (2 and 3), which, in a few days, become greenish-blue and more dense.

The next two members permanently retain their bulky blue character, and, even after being kept for many months, occupy four and a-half times the space occupied by the same amount of copper in the form of the less basic sulphates. If milk of lime, instead of lime-water, be used for preparing the more highly basic precipitates, they are invariably violet, instead of blue, this colour being, as we have reason to believe, distinctive of a cuprite.

The various members of the series, after precipitation, may be converted one into the other by the addition of more lime, or of more copper sulphate, although the conversion occupies some little time.

In column III is given the relative volume occupied by the various precipitates under similar conditions. This increases rapidly up to $10CuO,SO_3$, remains nearly constant to $10CuO,SO_3,3CaO$, and after decreasing graduallv for some distance, begins to fall rapidly.* The volume occupied by $5CuO,SO_3$ shows that it cannot be a mere mixture of the neighbouring compounds, for such a mixture would occupy 5·1 volumes, instead of 6·5; another series, quoted in the Woburn Report, illustrated this point more forcibly.

From column IV it will be seen that the least basic precipitates are sufficiently soluble in water for the amount of copper in solution to be determined by ferrocyanide; the solubility, however, extends considerably beyond this point, as is shown by the fact that the more basic liquids act on iron. Column IX contains the results of strictly comparable experiments wherein iron was left in the mixtures for two days. In this action, copper is first deposited on the metal, and then the solution becomes electrolysed, hydrogen being evolved and oxide of iron formed. This action goes on well beyond the point ($10CuO,SO_3$) at which the liquids become alkaline.

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* The series quoted in the Woburn Report were less complete, and the rapid decrease was erroneously taken as starting at $10CuO,SO_3,3CaO$.

In more strongly alkaline liquids—beyond $10CuO,SO_3,3CaO$—the iron gradually becomes dulled by the formation of a white deposit on it, which is probably a ferrite. Lime itself has no such action.

When the liquids containing these precipitates are boiled* (column VIII), no change takes place with the lower members, beyond that of the solids becoming more compact and green, as they do, also, on long keeping. As the basicity increases, a point is reached where boiling causes blackening of a portion of the precipitates, owing to the liberation of cupric oxide. With further increase in basicity, more of the precipitate blackens, the whole of it doing so at $10CuO,SO_3$; then the blackening diminishes, and ceases altogether at $10CuO,SO_3,3CaO$. At a further degree of basicity another change begins, this consisting of the precipitate becoming violet and dense, and eventually a point is reached where boiling again produces no change.

Up to a certain point dextrose has no action, and does not affect the solubility of the basic sulphate in the liquid (columns IV and V); but when a certain basicity is reached, we get, apparently, a direct action (column VI), the precipitates being reduced by the dextrose in the cold. This action is evidenced by the precipitates becoming in part of a dirty green colour, due to the mixture of cuprous oxide with the blue precipitate.

When a further degree of basicity is attained, an action of a totally different character occurs; the copper dissolves in the dextrose solution (column V); this becomes violet, and, after being kept for a certain time, turns yellow, owing to the spontaneous separation of cuprous oxide (column VI). The copper, while dissolved, is electronegative, and is absorbed by cellulose; it is present, no doubt, as cupridextrose.

When the basic sulphates are heated to boiling with dextrose solution, the action begins one stage earlier, column VII; the turning green of the undissolved precipitate occurs as soon as $5CuO,SO_3$ is passed, and the next stage consists of this same change, together with the dissolution of some of the precipitate, and the gradual deposition of an increasing amount of cuprous oxide from the solution: in the last stage the cuprous oxide is deposited entirely from the liquid.

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* They should have been prepared some time before boiling, or they may behave anomalously.

The evidence as to the individuality of the various compounds may be summarised as follows:

(1) $3CuO,SO_3$.—A greenish-blue precipitate, obtained by boiling copper sulphate solution (Pickering, *Chem. News*, 1883, **47**, 181). Also obtained by Shenstone (Trans., 1885, **47**, 375) in a crystalline condition by heating copper sulphate with a little water in sealed tubes at 200°; and by Friedel. Cesaro and Buttgenbach found it as a mineral. A series of experiments was made to ascertain whether this, or any less basic sulphate, was formed during the partial precipitation of copper sulphate by lime, but no such indications were obtained.

(2) $4CuO,SO_3,(0{\cdot}06CaSO_4)$.—A light blue precipitate, obtained by adding to copper sulphate alkalis in any quantity up to that sufficient to throw down all the metal; also as a crystalline precipitate by decomposing copper sulphate with an acetate (Pickering, *loc. cit.*); and as a crystalline mineral, bronchontite. It turns green on keeping or heating.

(3) $5CuO,SO_3,(0{\cdot}25CaSO_4)$.—Similar in character to the former. Its appearance coincides with the point (1) at which the copper in solution ceases to be recognisable by the ferrocyanide test (column IV in the table), (2) at which cupric oxide begins to be liberated on boiling (column VIII), and (3) at which cuprous oxide begins to separate when heated with dextrose (column VII). The volumes, also, show that it cannot be a mixture of the higher and lower sulphate.

(4) $10CuO,SO_3,1{\cdot}3CaSO_4$.—A full blue, bulky precipitate, the composition of which is established by its coinciding with the point at which the liquid becomes alkaline when alkali is added to copper sulphate; also by the action of dextrose in the cold, which, as soon as this point is past, begins to act on the precipitate, liberating cuprous oxide from it (column VI), or, when boiled with it, begins to dissolve some of the copper (column VII). The volumes (column III) also indicate its existence.

(5) $10CuO,SO_3,3CaO,CaSO_4$.—Composition proved by analyses in former communication, and also as being the point (1) up to which some copper is still in solution, as shown by the action of iron (column IX); (2) at which copper begins to dissolve in dextrose in the cold to form a violet solution, depositing cuprous oxide (column VI), and (3) at which boiling ceases to liberate cupric oxide (column VIII).

According to the analyses previously quoted, the composition of this precipitate remains constant with increasing amounts of lime, till the excess of the latter reaches a certain limit (about the point 5a in the table). The change in volumes (column III) and the results on boiling (column VIII) also indicate that some other, as yet unidentified, compound makes its appearance at this point.

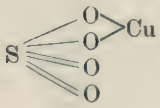
(6) CuO,2CaO.—Composition uncertain, see above.

(7) CuO,3CaO.—Approximate composition of the precipitate obtained on adding from 50 to 500 CaO to each molecule of copper sulphate.

(8) $15CuO,SO_3$. — A precipitate obtained by decomposing cuprammonium carbonate and sulphate with water (Pickering, Trans., 1909, **95**, 1417). Not fully examined.*

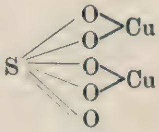
Developing a scheme for the representation of these various substances by the introduction of successive CuO groups into the molecule of copper sulphate, the introduction of one and two such groups gives the members A2 and A3, of which the latter is the lowest basic sulphate known, and is really the orthosulphate, the former being unknown, but analogous to the so-called monohydrate of the sulphate, in which, there can be little doubt, the water is not ordinary water of crystallisation. The introduction of further CuO groups would give the three members of the B series, and of these the first two have been isolated. The members of both these series should all exhibit similar properties, inasmuch as the copper in them is in the same condition. This is the case, for they all react with iron or ferrocyanide, and are not decomposed by dextrose:

A1.



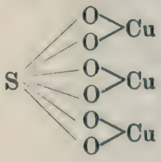
$CuSO_4$.

A2.



Not known (analogous to $CuSO_4,H_2O$).

A3.



$3CuO,SO_3$.

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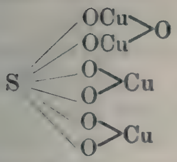
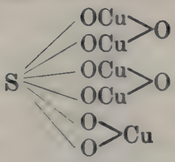
* It was suggested (Trans., 1907, **91**, 1995) that $10CuO,SO_3,10CaO,SO_3$ might exist; this was based on the view, which is now unacceptable, that the higher members of the series were molecular compounds of two basic sulphates of copper and calcium, the compound No. 5 (with the calcium sulphate added to it) being $10CuO,SO_3,4CaO,SO_3$.

B1.



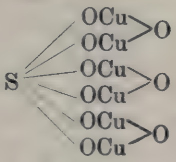
$4CuO,SO_3$.

B2.



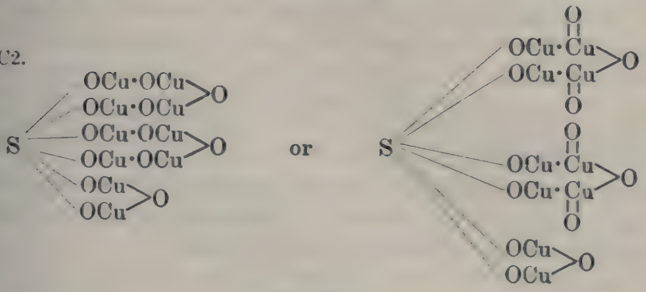
$5CuO,SO_3$.

B3.



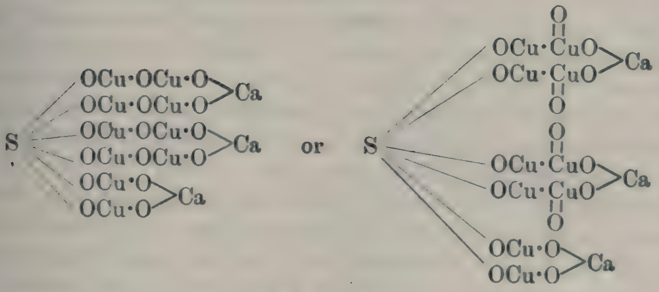
Not known.

C2.



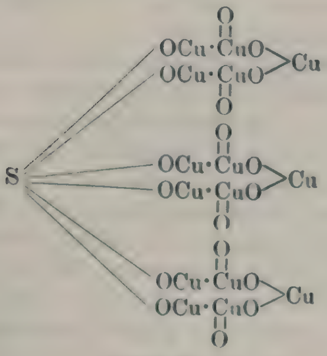
$10CuO,SO_3$.

F2.



$10CaO,SO_3,3CaO$.

F3.



$15CuO,SO_3$.

The introduction of further CuO groups may be effected in either of the ways indicated in C2, in the first of which the copper is dyad, and in the second, tetrad, as in the case of the cupri-salts. The second member of this series, containing two pairs of such CuO groups, corresponds with the next basic sulphate isolated. The ready separation of cupric oxide by heat from this compound (column VIII in the table) would be explained equally well by either of the formulæ, but its action on dextrose (column VII), analogous to that of the cupricitrates, seems to be best expressed by the second formula. Its small solubility, and feeble action on iron (column IX) is also more in consonance with this formula, which represents the presence of only one $\begin{matrix}-OCu\\-OCu\end{matrix}\!>\!O$ group, whereas, according to the first formula, there are three such groups present, and such a compound would be expected to act at least as energetically as the members of the B series.

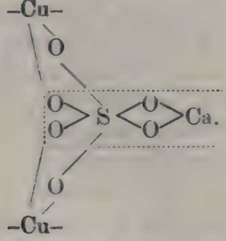
By the further action of an alkali, the external CuO groups would become converted into "cuprite" groups, as indicated in the alternative formulæ F2, which represent the next member of the series isolated. Such a substance would be analogous to the γ-cupri-compounds, and, like these, it dissolves in dextrose solution, forming a blue liquid, from which cuprous oxide is deposited (column VII), and which combines with cellulose. The basic sulphate obtained by the decomposition of cuprammonium sulphate fits in as the third member of this series, F3.

Although the members of the F series are less stable in the presence of dextrose than are those of the preceding series, in consequence of their containing the cuprite groups, they are more stable under the action of heat, the external CuO groups being hedged in, as it were, by the outlying electropositive element. The remarkable differences in behaviour of the various basic sulphates on being heated is thus explained.

The series F is derived from the series C by the introduction of $3M''O$, and there might be two intermediate series with $M''O$ and $2M''O$, respectively. That some other compounds exist which have not been isolated is almost certain, as has already been pointed out.

The final products of the action of lime on copper sulphate seem to be simple cuprites, and the oxidising action of these on dextrose is still more energetic than that of highest basic sulphate.

Two members of the sulphate series, C2 and F2, contain a considerable proportion of combined calcium sulphate; the presence of this can be explained if the alternative formulæ are adopted, but not otherwise, the calcium sulphate becoming an orthosulphate by connexion with two ⁚CuO groups of the quadrivalent copper:



The maximum amount of sulphate thus capable of being introduced would be two molecules, and this is the amount actually found when the basic sulphate F2 is precipitated in the presence of excess of sodium sulphate, its composition then being

$$10CuO,SO_3,3CaO,2(Na_2Ca)SO_4$$

(*loc. cit.*).

Ferrites.

How far the explanation which seems to be satisfactory with the copper compounds will apply to those of other metals remains to be seen; but, in the case of iron, some evidence has been obtained that an analogy exists.

In a paper on emulsions (Trans., 1907, **91**, 2001) it was mentioned that when ferrous sulphate is precipitated by excess of lime, and churned up with paraffin, the greenish-black precipitate of basic sulphate often becomes quite white, or does so when the emulsion is kept for some time. This was attributed to the chemical action of some impurity in the oil; but it has since been found that the same change occurs, although much more slowly, when the basic sulphate is left with milk of lime only, or even with excess of clear lime-water, decolorisation in that case requiring many days to become complete. The white substance retains the flocculent character of the basic sulphate, and remains quite unchanged in a closed vessel, but when exposed to the air it very gradually becomes orange, through the formation of ferroso-ferric oxide. On digestion with a solution of dextrose, a small portion of it dissolves, and in this the iron is in the electronegative condition, as it gives no blue colour with ferrocyanide until acid is added.

To obtain some information on the subject, quantities of one litre of lime-water, diluted with 20 per cent. of water, were mixed with different amounts of ferrous sulphate, and left in closed bottles for six weeks, after which the lime still in solution was determined. In this way the molecular proportions of lime used up in the precipitation of the iron were determined, and these are given in the accompanying table. The proportions of lime to iron taken are also given, and, as will be seen, the lime in all cases was in excess. It was only in the last three experiments that the greenish-black basic sulphate became white; it very nearly did so in No. 4, whilst in No. 3 there was a smaller, but still considerable, lightening in colour. Taking the last three experiments, where the change was complete, the proportion of lime used up is evidently in excess of the one molecule which would suffice for the complete decomposition of the ferrous sulphate, so that some of the lime must have gone into combination with the ferrous oxide. Omitting the last experiment, as being uncertain owing to the very small proportions in which the iron had to be taken, the excess of lime used is 0·27CaO, which would indicate the formula of the compound as 4FeO,CaO, if no sulphur is left in it; this, however, was not the case, for, in No. 5, there was found to be $0·153SO_3$ present to each atom of iron, and in No. 6, $0·05SO_3$; this may be present simply as calcium sulphate, but, if it is combined with the iron in the form of a basic sulphate, the proportions of FeO to CaO in the precipitate would be less than the 4 : 1 mentioned above.

Precipitation of Ferrous Sulphate by Lime.

	Proportions taken. Fe : CaO.	Proportions used up. Fe : CaO.
1.	1 : 1·033	1 : 0·334
2.	1 : 2·07	1 : 0·543
3.	1 : 5·15	1 : 0·641
4.	1 : 10·3	1 : 1·030
5.	1 : 25·8	1 : 1·232
6.	1 : 51·5	1 : 1·311
7.	1 : 103·0	1 : 1·116

Further work would be required, of course, before the nature of the substances here present could be established, but it is evident that ferrous compounds analogous to the alkaline basic salts of copper or to the cuprites do exist, and it is noticeable that their formation seems to necessitate approximately the same large excess of alkali, for with the iron compound between 10 and 26 equivalents of lime to each equivalent of iron are required, whilst in the case of copper, about 25 equivalents were necessary (*loc. cit.*).

The solubility of basic metallic salts of this description in organic substances probably plays an important part in their assimilation by plants.

HARPENDEN.

The Council has ordered the following letter and report to be printed in the Journal and Proceedings of the Society:

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON,
LONDON, S.W.
August 22nd, 1910.

GENTLEMEN,

I beg to forward the Annual Report of the International Committee on Atomic Weights for 1911, to which I have appended, by their desire, the signatures of Professors Ostwald and Urbain.

The Committee, it will be seen, have acceded to the wish of the Council of the Chemical Society, and have prepared the Report in such time that it can be published prior to the commencement of the ensuing academic year.

Slight changes have been made in the atomic weights of argon, helium, krypton, lithium, neon, phosphorus, platinum, strontium, vanadium, and xenon, but otherwise the new table remains very much as in 1910.

I have the honour to be, Gentlemen,
Your obedient servant,
T. E. THORPE.

To the Hon. Secretaries,
The Chemical Society,
Burlington House,
London, W.

Report of the International Committee on Atomic Weights, 1911.

In the autumn of 1909 the Council of the Chemical Society of London voted unanimously in favour of issuing the annual report of the International Committee on Atomic Weights in September or October instead of in January as heretofore. In that proposition the Chemical Society of France has concurred, and American sentiment has also been favourable to the suggested change. Therefore the change is now made.

The reasons offered for the new policy are very simple. First, the school year, at least in most educational institutions, begins in the autumn. It is desirable that teachers should then have the latest table of atomic weights at their command, in order to avoid changes after school work has begun. Secondly, publishers of text-books are accustomed to issue their new works in the autumn, and often request early information as to changes which are likely to be made. The proposed change in the time of issuing the table is therefore an aid to teachers, students, and publishers, and no disadvantage to anyone else. The immediate usefulness of the table is increased, and to attain that end should be the main purpose of the Committee.

Since the preparation of the report for 1910, a number of important memoirs upon atomic weights have appeared. The results obtained are, in brief, as follows:

Chlorine.—The density, composition by volume, and compressibility of hydrochloric acid have been measured by Gray and Burt (Trans., 1909, **95**, 1633) with great care. From the density and volumetric composition, when H = 1·00762, Cl = 35·459. From the density and compressibility, Cl = 35·461. The mean, 35·460, is the value given in the annual table of atomic weights for the past two or three years.

The density of hydrochloric acid has also been determined by Scheuer (*Zeitsch. physikal. Chem.*, 1909, **68**, 575), who gives measurements made under varying conditions. His final conclusion, based upon his own work after comparison with that of Gray and Burt, is that Cl = 35·466.

Lithium.—Richards and Willard (*J. Amer. Chem. Soc.*, 1910, **32**, 4), in their important research upon the atomic weight of lithium, measured three distinct ratios, namely, silver to lithium chloride, silver chloride to lithium chloride, and lithium perchlorate to lithium chloride. From these ratios, without the intervention of any others, the following independent values for three atomic weights are obtained:

Li = 6·939.
Cl = 35·454.
Ag = 107·571.

The value for silver varies from the accepted value, 107·88, by about one part in 12,000, which is probably less than the actual uncertainty. That for chlorine diverges more widelv, namely, by about one part in 6000. The new figures are undoubtedly entitled to great weight, but in view of the excellent work done by others it would be unwise to make any hasty change in the table. For lithium, however, the value 6·94 may be taken, replacing the old 7·00.

Strontium.—Thorpe and Francis (*Proc. Roy. Soc.*, 1910, **83**, *A*, 277), in their determinations of the atomic weight of strontium, measured six ratios, and obtained the following results:

Ratio $2Ag$ to $SrBr_2$	$Sr = 87\cdot645$
,, $2AgBr$ to $SrBr_2$	,, $= 87\cdot653$
,, $2Ag$ to $SrCl_2$	,, $= 87\cdot642$
,, $2AgCl$ to $SrCl_2$	,, $= 87\cdot645$
,, $SrBr_2$ to $SrSO_4$	,, $= 87\cdot629$
,, $SrCl_2$ to $SrSO_4$	,, $= 87\cdot661$
Mean of all	$Sr = 87\cdot646$

The value adopted by the authors is 87·65. Richards's figure is 87·62. An intermediate value, 87·63, is adopted in the new table.

Phosphorus.—Atomic weight redetermined by Baxter and Jones (*J. Amer. Chem. Soc.*, 1910, **32**, 298). From the ratio between silver and silver triphosphate, the authors find $P = 31\cdot043$, when $Ag = 107\cdot88$. The rounded-off figure 31·04 is to be adopted.

Vanadium.—From the ratio between silver chloride and vanadyl trichloride, Prandtl and Bleyer (*Zeitsch. anorg. Chem.*, 1910, **65**, 152) find $V = 50\cdot963$ and $51\cdot133$ in two series of experiments. In a later paper, Prandtl and Bleyer (*Zeitsch. anorg. Chem.*, 1910, **67**, 257), also from analyses of vanadyl trichloride, find $V = 51\cdot061$. From reductions of V_2O_5 to V_2O_3, they found $V = 51\cdot374$. The latter method, however, they regard as uncertain. The value $V = 51\cdot06$ may be provisionally adopted.

Tellurium.—Marckwald and Foizik (*Ber.*, 1910, **43**, 1710; see also Browning and Flint, *Amer. J. Sci.*, 1909, [iv], **28**, 347, who adduce evidence to show that tellurium is possibly complex), by a somewhat complex volumetric process, based on the oxidation of TeO_2 by $KMnO_4$, conclude that $Te = 127\cdot61$. This agrees with many of the other recent determinations of the constant, but is not sufficiently exact to supplant the value given in the table.

Rhodium.—Two inaugural dissertations upon the atomic weight of rhodium have been issued from Gutbier's laboratory at Erlangen. Renz reduced rhodium pentamine bromide in hydrogen and found $Rh = 102\cdot92$. H. Dittmar (reproduced in *Sitzungsber. phys. med. Soz. Erlangen*, **40**, 184), by similar reductions of the corresponding chloride, found $Rh = 102\cdot93$.

Platinum.—The very elaborate investigation of Archibald (*Proc. Roy. Soc. Edin.*, 1909, **29**, 721) upon the atomic weight of platinum was based upon analyses of the chloroplatinates and bromoplatinates of potassium and ammonium. In all, 28 ratios were measured, giving values for Pt ranging between 195·19 and 195·25. Their arithmetical mean gives $Pt = 195\cdot22$. Archibald, however, in his final discussion, uses only 12 ratios, giving, in mean, Pt = 195·23. The figure 195·2 is given in the table.

The Inert Gases.—The densities and molecular weights of helium and neon have been redetermined by Watson (Trans., 1910, **97**, 810). For the atomic weights he finds He = 3·994 and Ne = 20·200. In another paper (*ibid.*, **97**, 833) he applies the critical constants of krypton and xenon to their densities as determined by Moore, and finds Kr = 82·92 and Xe = 130·22. There are also new determinations of the density of argon by Fischer and Hehnel (*Ber.*, 1910, **43**, 1435). Their mean value, referred to O = 16, is 19·945, a figure rather higher than that given by Ramsay and Travers. It corresponds to an atomic weight of A = 39·89.

It is also to be noted that a third, revised edition of Clarke's "Recalculation of the Atomic Weights" has recently been published by the Smithsonian Institution.

The annual table of atomic weights for 1911 follows, with but few changes from that of the preceding year.

F. W. CLARKE.
W. OSTWALD.
T. E. THORPE.
G. URBAIN.

1911.

International Atomic Weights.

		O = 16.			O = 16.
Aluminium	Al	27·1	Molybdenum	Mo	96·0
Antimony	Sb	120·2	Neodymium	Nd	144·3
Argon	A	39·88	Neon	Ne	20·2
Arsenic	As	74·96	Nickel	Ni	58·68
Barium	Ba	137·37	Nitrogen	N	14·01
Bismuth	Bi	208·0	Osmium	Os	190·9
Boron	B	11·0	Oxygen	O	16·00
Bromine	Br	79·92	Palladium	Pd	106·7
Cadmium	Cd	112·40	Phosphorus	P	31·04
Cæsium	Cs	132·81	Platinum	Pt	195·2
Calcium	Ca	40·09	Potassium	K	39·10
Carbon	C	12·00	Praseodymium	Pr	140·6
Cerium	Ce	140·25	Radium	Ra	226·4
Chlorine	Cl	35·46	Rhodium	Rh	102·9
Chromium	Cr	52·0	Rubidium	Rb	85·45
Cobalt	Co	58·97	Ruthenium	Ru	101·7
Columbium	Cb	93·5	Samarium	Sa	150·4
Copper	Cu	63·57	Scandium	Sc	44·1
Dysprosium	Dy	162·5	Selenium	Se	79·2
Erbium	Er	167·4	Silicon	Si	28·3
Europium	Eu	152·0	Silver	Ag	107·88
Fluorine	F	19·0	Sodium	Na	23·00
Gadolinium	Gd	157·3	Strontium	Sr	87·63
Gallium	Ga	69·9	Sulphur	S	32·07
Germanium	Ge	72·5	Tantalum	Ta	181·0
Glucinum	Gl	9·1	Tellurium	Te	127·5
Gold	Au	197·2	Terbium	Tb	159·2
Helium	He	3·99	Thallium	Tl	204·0
Hydrogen	H	1·008	Thorium	Th	232·0
Indium	In	114·8	Thulium	Tm	168·5
Iodine	I	126·92	Tin	Sn	119·0
Iridium	Ir	193·1	Titanium	Ti	48·1
Iron	Fe	55·85	Tungsten	W	184·0
Krypton	Kr	82·9	Uranium	U	238·5
Lanthanum	La	139·0	Vanadium	V	51·06
Lead	Pb	207·10	Xenon	Xe	130·2
Lithium	Li	6·94	Ytterbium (Neoytterbium)	Yb	172·0
Lutecium	Lu	174·0	Yttrium	Y	89·0
Magnesium	Mg	24·32	Zinc	Zn	65·37
Manganese	Mn	54·93	Zirconium	Zr	90·6
Mercury	Hg	200·0			

CXCIX.—*Optically Active Salts of 4-Oximinocyclohexanecarboxylic Acid and the Configuration of the Oximino-Group.*

By William Hobson Mills and Alice Mary Bain.

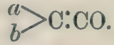
The theory which Hantzsch and Werner put forward (*Ber.*, 1890, **23**, 11) to account for the isomerism of the oximes provides so satisfactory and consistent an explanation of the facts that it has received practically universal acceptance. The fundamental assumption, however, on which this theory is based—namely, that in the oximino-group the three valencies of the nitrogen atom are not in one plane—has rested up to the present on indirect evidence only.

It seemed to us that it might be possible to put this hypothesis to direct experimental test by investigating an oximino-compound so constituted that its molecule would possess a plane of symmetry or not according as the oximino-group has a plane or a trihedral configuration.

This condition is fulfilled by compounds of the type:

$$\begin{matrix}a\\b\end{matrix}\!>\text{C:C:NOH},$$

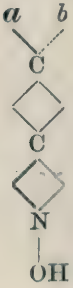
which might be regarded as oximes of the unsymmetrical ketens:



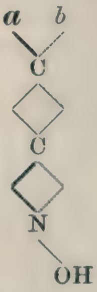
$$\begin{matrix}a\\b\end{matrix}\!>\text{C:CO}.$$

A molecule of the configuration (I) is clearly superposable on its mirror-image, whilst one of configuration (II) is not.

(I.)



(II.)

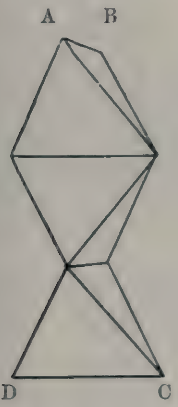


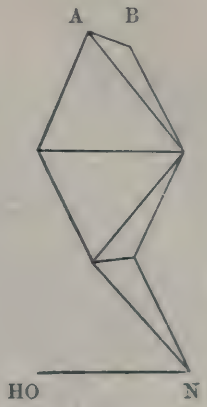
In these diagrams the dotted lines are intended to indicate valencies lying behind the plane of the paper, while valencies in front of it are represented by thick lines.

A substance of configuration (II) stands in close relationship to allene derivatives of the type:

$$\begin{matrix}a\\b\end{matrix}\!>\!C{:}C{:}C\!<\!\begin{matrix}c\\d,\end{matrix}$$

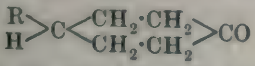
the molecular asymmetry of which was first pointed out by van't Hoff in 1875 (*La Chimie dans l'Espace*, p. 29), for, provided that the oximino-group has the configuration assumed by Hantzsch and Werner, it can be substituted for one of the carbon atoms of such an allene compound, as shown in the diagram, without destroying the asymmetry of the molecule:



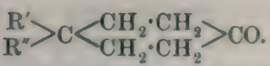


The preparation and manipulation of a compound of this type would doubtless offer even greater difficulties than those which have hitherto prevented the experimental realisation of van't Hoff's prediction in its original form (see Dimroth and Feuchter, *Ber.*, 1903, **36**, 2238; Lapworth and Wechsler, Trans., 1910, **97**, 38).

These difficulties can, however, be avoided by means of the same device as has been successfully employed by Perkin and Pope (Trans., 1908, **93**, 1075; Perkin, Pope, and Wallach, Trans., 1909, **95**, 1789; compare Marckwald and Meth, *Ber.*, 1906, **39**, 1171) in order to obtain a compound (methyl*cyclo*hexylidene-4-acetic acid) which reproduces the essential spatial characteristics of the allene derivatives without having their instability—that is, by the expansion of the two-membered ethylene ring into the hexamethylene ring. In place of keten oximes, one then has the oximes of substituted *cyclo*hexanones of the types:

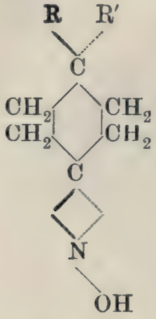


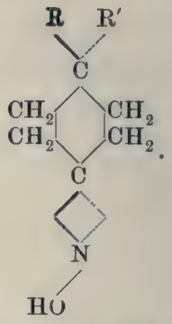
$$\begin{matrix}R\\H\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!>\!CO$$



$$\begin{matrix}R'\\R''\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!>\!CO.$$

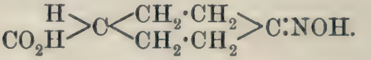
If the three valencies of the nitrogen atom in the oximino-group are not in one plane, then the oxime of such a ketone must consist of an equimolecular mixture of two enantiomorphous forms:





If, on the other hand, they are in one plane, these oximes, like the ketones from which they are derived, will have a plane of symmetry, and will therefore be incapable of exhibiting optical activity. Hence, if a compound of such constitution can be obtained in an optically active condition, it will follow as a necessary consequence that the three valencies of the nitrogen atom in the oximino-group do not lie in one plane.

In order to facilitate resolution, it is desirable that the substance should contain the carboxyl group. The simplest compound of the necessary type is therefore:



$$\begin{matrix}H\\CO_2H\end{matrix}\!>C<\!\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!>C{:}NOH.$$

This is the oxime of the important *cyclo*hexanone-4-carboxylic acid which was synthesised by W. H. Perkin, jun. (Trans., 1904, **85**, 416), and served as the basis of his well-known syntheses of terpin, terpineol, and dipentene (Trans., 1904, **85**, 654). It has also been obtained by Lumsden (Trans., 1905, **87**, 87) by the reduction of anisic acid. It is shown in the present communication that this oximino-acid (or rather its salts) is, in fact, capable of existing in two enantiomorphously related forms, the separation of which has been effected with the aid of morphine and quinine.

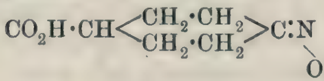
If a molecular proportion of morphine is added to the ethyl-alcoholic solution of the acid, a morphine salt separates which contains a dextrorotatory form of the acid, for on decomposing it with excess of ammonia and suitably removing the morphine, the ammonium salt which remains in the solution is strongly dextrorotatory. The ammonium salt prepared in this manner has a molecular rotation $[M]_D$ in aqueous solution varying from about 50° to 60° in different preparations. By means of quinine the corresponding lævorotatory ammonium salt has similarly been obtained, the salt which the *l*-acid forms with the alkaloid being in this case the more sparingly soluble of the two diastereoisomerides. This lævorotatory ammonium salt has a molecular rotation of $[M]_D -70^\circ$ to -80° in aqueous solution; the separation effected by quinine is thus more complete than that attained with the aid of morphine. The activity of these salts is evanescent, and its rate of disappearance falls off in accordance with the unimolecular formula, the velocity constants being very different for different salts of the acid. The rate of racemisation is greater, in the salts investigated, the weaker the base from which the salt is derived, and the presence of an excess of alkali, which in so many cases accelerates racemisation, here greatly retards it, while acidification causes the rapid disappearance of the rotatory power. Thus the morphine salt of the *d*-acid when dissolved in water shows mutarotation, obviously on account of the rapid diminution of the dextrorotation due to the acid, the period of half-change being about one minute. For an approximately $0{\cdot}2N$-solution of the ammonium salt in water, the time of half racemisation is thirteen minutes, and for the sodium salt under similar conditions twenty-four minutes. The presence of ammonia in $N/10$-concentration increases the persistence of the activity of the ammonium salt approximately forty-fold, raising the period of half-change to 8·5 hours, and a corresponding addition of sodium hydroxide to the solution of the sodium salt has a still greater relative effect on the rate of racemisation, lengthening the period of half-change from twenty-four minutes to twenty-two hours.

The rapid racemisation of the salts of the acid with weak bases renders intelligible the results observed in preparing the morphine and quinine salts from the inactive acid. In the case of the latter salt, for example, the crystals which separate yield a lævorotatory ammonium salt after decomposition with ammonia and removal of the quinine, but there is no corresponding amount of quinine *d*-acid salt in the mother liquor, the solution of ammonium salt, obtained after removal of the quinine from the latter, being quite inactive. However, on concentration of the mother-liquor, another crop of quinine *l*-acid salt is deposited of similar activity to the first, and so on. The behaviour of the morphine salt is analogous—not only the first crystallisation, but also the subsequent crops obtained on concentration of the alcoholic mother liquor all yield solutions of dextrorotatory ammonium salt after removal of the morphine.

The process therefore appears to be one of activation rather than of simple resolution, and recalls the behaviour of the methylethylpropyl tin *d*-camphorsulphonate and bromocamphorsulphonate described by Pope and Peachey (Proc., 1900, **16**, 42, 116).

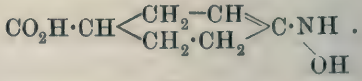
It seemed inevitable from the foregoing that any attempts to isolate the optically active forms of the acid itself would be unsuccessful. It was therefore necessary, in order to make these experiments as conclusive as possible, to obtain some definite proof that the substances, to which these optically active solutions owe their rotatory power, are indeed the normal ammonium salts of dextro- and lævo-rotatory forms of oximino*cyclo*hexane-4-carboxylic acid. This was done by treating the active solutions with an aqueous solution of silver nitrate. The substances thus precipitated, from the dextro- as well as from the lævo-rotatory solutions, were found to be normal silver salts of this acid in analytically pure condition. Further, they were optically active, for on treating them with an aqueous solution of sodium chloride, the solutions of sodium salt obtained were respectively dextro- and lævo-rotatory, the rotations observed corresponding with molecular rotations $[M]_D$ 74·5° and −79·9° respectively.

These results show conclusively that the salts of this oxime-acid are capable of existing in two enantiomorphously related forms. Moreover, the evanescent character of the optical activity makes it certain that their molecular asymmetry is determined in some manner by the oximino-group. It remains to be considered whether any method of accounting for the asymmetry is possible other than that indicated at the beginning of this paper. Apparently the only other hypothesis by which it might, at first sight perhaps, appear explicable is that the compound can exist in the two tautomeric forms (III) and (IV), and that the optically active salts are derived from the latter, which contains an ordinary asymmetric carbon atom:



$$CO_2H\cdot CH{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}C{:}N\cdot OH$$

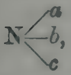
(III.)



$$CO_2H\cdot CH{<}\begin{matrix}CH_2-CH\\ CH_2\cdot CH_2\end{matrix}{>}C\cdot NH\cdot OH$$

(IV.)

This explanation, however, cannot be maintained. If the active compound has the formula (IV), it is a β-substituted hydroxylamine, and must possess the power of reducing Fehling's solution, which is characteristic of compounds of this class. A comparison of the behaviour of an active solution in this respect with that of acetoxime on the one hand, and of β-phenylhydroxylamine on the other, showed that although its reducing power was slightly greater than that of acetoxime, it was of an altogether different order from that of phenylhydroxylamine, and it is quite certain that no appreciable quantity of a β-substituted hydroxylamine could have been present in the solution.

The conclusion therefore seems unavoidable that the molecular asymmetry, to which these salts owe their optical activity, is determined by the peculiar configuration of the doubly linked tervalent nitrogen atom. They accordingly constitute a new type of optically active substances; and through their optical activity a direct experimental proof is afforded that the three valencies of tervalent nitrogen, however they may be disposed in a compound of the type  $\mathrm{N}\begin{array}{l}\diagup a\\ -b\\ \diagdown c\end{array}$, are directed in the oximino-group, as was postulated by Hantzsch and Werner, along the three edges of a trihedral angle.

These substances may also possess a certain interest in that they provide another example of compounds of which, like *d*- and *l*-inositol,* and *d*- and *l*-1-methyl*cyclo*hexylidene-4-acetic acids (Perkin, Pope, and Wallach, *loc. cit.*), the molecular asymmetry is more fittingly defined with reference to the configuration of the molecule as a whole than expressed in terms of the presence of some "asymmetric atom."

EXPERIMENTAL.

The *cyclo*hexanone-4-carboxylic acid employed for the preparation of the oxime the properties of which form the subject of this communication, was synthesised according to the method described by W. H. Perkin, jun. (*loc. cit.*), and Kay and Perkin (Trans., 1906, **89**, 1640). The acid was converted into its oxime by mixing its solution in ten parts of absolute alcohol with one molecular proportion of hydroxylamine hydrochloride dissolved in about an equal volume of the same solvent, and adding one molecular proportion of anhydrous sodium acetate. After three days an equal volume of dry ether was added, the precipitated sodium chloride was removed, and the solution then evaporated, finally in an exhausted desiccator. The oximino-acid was extracted from the solid residue in a Soxhlet apparatus, and purified by recrystallising from dry ether in the same manner. It separates from ether in crystalline crusts, melting at 148—148·5°, and otherwise agreeing with Perkin's description (*loc. cit.*).

*Quinine Salts of Oximino*cyclo*hexane-4-carboxylic Acid.*

A quinine salt containing a preponderance of the lævorotatory form of the acid may be obtained by heating the solution of the inactive acid in 30 parts of water with 2·1 parts (slightly more than one molecular proportion) of anhydrous quinine, the small excess of quinine being removed by filtration of the hot liquid. The salt separates on cooling, usually in hemispherical clusters of fine needles. After being air-dried, it contains 2½ molecules of water of crystallisation:

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* The configuration of the active inositols was, apparently, first given in *Stereochemie* (van't Hoff-Meyerhoffer, 1892), p. 91; see also Bouveault, *Bull. Soc. chim.*, 1894, [iii], **11**, 145.

1·2756 air-dried salt lost 0·1070 H_2O. $H_2O = 8·39$.
1·0693 „ „ „ 0·0894 H_2O. $H_2O = 8·36$.
$C_{27}H_{35}O_5N_3,2\frac{1}{2}H_2O$ requires $H_2O = 8·56$ per cent.

Under the above conditions, approximately 80 per cent. of the total quantity of salt crystallises out. Recrystallisation can be conveniently effected from 10 parts of hot water.

The investigation of the optical activity of the acid component of the salt was carried out by placing a weighed quantity of the salt (0·3 to 0·5 gram) in a small separating funnel, and adding 10 c.c. of an aqueous solution of sodium or ammonium hydroxide of such concentration that the amount of alkali left after decomposition of the salt would give an approximately $N/10$-solution. The quinine was then completely removed by extracting three times with chloroform, 12—15 c.c. of chloroform being used for each extraction. The alkaline solution of the sodium or ammonium salt was then filtered, and after washing the separating funnel and filter with successive small quantities of $N/10$-sodium or ammonium hydroxide, as the case might be, the mixed filtrate and washings were examined polarimetrically. For example, 0·66 gram of air-dried quinine salt was treated with an aqueous solution (10 c.c.) of 0·12 gram of sodium hydroxide. After proceeding in the above manner, the following polarimetric observation was made, the final volume of the aqueous solution being 14·00 c.c.:

$$l = 2,\ c^* = 1·606,\ \alpha_D\ -1·47°,\ [M]_D\ -81·9°.$$

On examination of the various preparations of quinine salt in this manner, it was found that the sodium or ammonium salts obtained from them possessed molecular rotations lying for the most part between $[M]_D\ -70°$ and $[M]_D\ -80°$.

It was naturally useless to attempt to obtain the optically pure quinine *l*-acid salt by repeated recrystallisation in the usual way, since it is clear from the observations described below (pp. 1880, 1881) that even with the most rapid working it must be impossible to avoid racemising the salt extensively with regard to its acid component every time that it is brought into solution. The conditions were rather to be sought under which the pure salt would crystallise out directly free from its diastereoisomeride. These should presumably be such as would secure that the rate of racemisation should be a maximum compared with that of crystallisation, since in this manner the concentration of quinine *l*-acid salt would be kept as high, and that of quinine *d*-acid salt as low as possible during the crystallisation. Accordingly, it was endeavoured to diminish the rate of crystallisation by slow cooling and accelerate that of racemisation by acidification, and, in fact, although the experiments in this direction are not complete, the salt of highest activity (with regard to the acid component) hitherto observed was obtained by crystallisation from a solution somewhat strongly acidified with acetic acid, the sodium salt prepared from it having given the following numbers:

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* The concentrations given throughout this paper refer to the sodium or ammonium salt present in the solution examined. They are calculated from the amount of quinine or other salt taken.

$$l=2,\ c=0{\cdot}727,\ \alpha_D\ -0{\cdot}74^\circ,\ [M]_D\ -91{\cdot}0^\circ.$$

In preparing the quinine *l*-acid salt from inactive acid, it is found that the excess of the dextrorotatory form of the acid, which should be present in the mother liquor in order to correspond with the excess of the lævorotatory form removed from the solution in combination with quinine, has disappeared, for the mother liquor (at any rate if a short time is allowed to elapse before its separation and examination) contains the quinine salt of the inactive acid only, since after the addition of a small excess of sodium hydroxide solution and removal of the quinine by chloroform, the solution of sodium salt obtained is inactive. On concentrating the mother liquor, the second crop of quinine salt obtained contains again an excess of the *l*-acid salt. For example, after converting 3·2 grams of inactive acid into quinine salt in the manner described above, the crop, which crystallised directly, weighed 8·5 grams (about 80 per cent. of the total quantity of salt produced) and gave rise to sodium salt of molecular rotation $[M]_D\ -71{\cdot}5^\circ$ ($c=0{\cdot}731$). The second crop, obtained by concentrating the mother liquor, weighed 0·96 gram (another 10 per cent. of the total quantity of salt), and gave rise to sodium salt of molecular rotation $[M]_D\ -81{\cdot}9^\circ$ ($c=1{\cdot}607$).

These results are clearly due to the racemisation phenomena which have already been mentioned. Of the two diastereoisomeric quinine salts, that of the *l*-acid must be the less soluble in water, and thus crystallises first from an aqueous solution containing equal quantities of the two salts. The excess of quinine *d*-acid salt thereby left in solution, however, racemises very rapidly, so that in spite of the removal of the quinine *l*-acid salt, an approximate equality is maintained between the quantities of the two salts in the solution. An excess of the quinine *l*-acid salt is accordingly deposited throughout the process of crystallisation.

In our earliest experiments (Proc., 1909, **25**, 177) the quinine *l*-acid salt was obtained by combining the inactive acid with quinine in ethyl acetate solution and allowing crystallisation to take place from that solvent. This procedure was abandoned, since it was found that this salt could be obtained more rapidly and certainly, and, moreover, in a state of higher optical activity, by using water as solvent. These experiments were, however, of some interest, since by means of them not only the quinine *l*-acid salt, but also in some cases a salt containing a preponderance of the diastereoisomeric quinine *d*-acid salt was obtained. Thus, in one experiment, 5·4 grams of quinine (anhydrous) were dissolved in 300 c.c. of dry ethyl acetate, and to the boiling solution 2·61 grams (one molecular proportion) of the finely powdered acid were added. The quinine salt formed separated very slowly. After five days it was collected, and a portion dried in a vacuum was polarimetrically examined in solution in ethyl acetate, racemisation taking place in this solvent far more slowly than in water or in alcohol:

$$l=2\,;\ c=1\cdot6512\,;\ \alpha_{D}^{18}\ -3\cdot24^\circ\,;\ [\alpha]_{D}^{18}\ -98\cdot1^\circ.$$

Since the specific rotation in ethyl acetate of the quinine salt of the inactive acid (prepared by dissolving 0·2732 gram of anhydrous quinine and 0·1324 gram of the acid in 25 c.c. of ethyl acetate) was found to be as follows:

$$l=2\,;\ c=1\cdot6224\,;\ \alpha_{D}^{12}\ -4\cdot28^\circ\,;\ [\alpha]_{D}^{12}\ -131\cdot9^\circ$$

the acid component of the salt was clearly markedly dextrorotatory. On recrystallisation of this preparation from ethyl acetate, some of the dextrorotatory power was, however, lost, the specific rotation having risen to $[\alpha]_{D}^{16}$ $-106\cdot5^\circ$. The dextrorotatory ammonium salt obtained from this quinine salt was examined with the following result:

$$l=2,\ c=0\cdot947,\ \alpha_{D}\ 0\cdot44^\circ,\ [M]_{D}\ 40\cdot4^\circ.$$

These results recall the interesting observations recently made by McKenzie and Clough (Trans., 1909, **95**, 783) on the crystallisation of the morphine salt of phenylchloroacetic acid, a given ethyl-alcoholic solution of morphine (1 mol.) and *r*-acid (2 mols.) depositing either morphine *d*-acid or morphine *l*-acid salt, according to the exact conditions under which crystallisation takes place.

Silver 1:4-*Oximino*cyclo*hexanecarboxylate.*—To the solution of ammonium *l*-acid salt, obtained by adding a solution of 0·348 gram of ammonia in 14 c.c. of water to 6·61 grams of quinine *l*-acid salt, and removing the quinine by extracting with chloroform, an aqueous solution of 2·75 grams of silver nitrate was added. The dense precipitate of silver salt thus produced was collected, thoroughly washed with water, rapidly passed out on a porous tile, and then dried for five days over sulphuric acid in an exhausted desiccator, the whole of the operations being carried out in non-actinic light. 2·20 Grams of silver salt were thus obtained in the form of a white powder, which apparently can be preserved indefinitely if protected from light. On being gently heated, it decomposes almost explosively, but if mixed with a large proportion of powdered cupric oxide, its analysis presents no special difficulty:

0·3860 gave 0·4542 CO_2 and 0·1368 H_2O. C = 32·09; H = 3·94.
0·2783 „ 13·35 c.c. N_2 at 24° and 760 mm. N = 5·37.
0·2978 „ 0·1616 AgCl. Ag = 40·85.
$C_7H_{10}O_3NAg$ requires C = 31·82; H = 3·79; N = 5·30;
Ag = 40·90 per cent.

This silver salt is too sparingly soluble to allow of its rotatory power being measured directly. It was, however, possible to demonstrate its optical activity by converting it into sodium salt and determining the rotatory power of the latter. Dry silver salt (0·8901 gram) was digested with 7 c.c. of an aqueous solution of sodium chloride containing 4·4 grams of sodium chloride and 0·4 gram of sodium hydroxide in 100 c.c., the sodium hydroxide being added in order to check the racemisation of the dissolved sodium salt, which proceeds rapidly in neutral solution (see p. 1877). The resulting solution was decanted from the solid residue through a filter, the residue repeatedly extracted in the same way with successive small quantities of the alkaline solution of sodium chloride, and the total filtrate polarimetrically examined:

$$l = 2,\ c = 0{\cdot}4065,\ \alpha_D\ -3{\cdot}82^\circ,\ [M]_D\ -79{\cdot}9^\circ.$$

Morphine d-*Oximino*cyclo*hexane-4-carboxylate.* — When equimolecular proportions of morphine and oximino*cyclo*hexane-4-carboxylic acid are mixed in hot ethyl-alcoholic solution, the sparingly soluble morphine salt which separates contains a preponderance of the dextrorotatory form of the acid. 5·8 Grams of the acid, dissolved in 50 c.c. of absolute alcohol, were added to a hot solution of 11·19 grams of morphine in 200 c.c. of the same solvent. The salt (14·04 grams) was gradually deposited, on cooling, in rosettes of small prisms. It can be recrystallised from about 30 parts of boiling absolute alcohol. It can also be recrystallised from methyl alcohol, but it is very sparingly dissolved by ethyl acetate, chloroform, or other common organic solvents, although easily soluble in cold water. The optical activity of the acid component of the salt was examined in a manner similar to that employed in the case of the quinine salt. The very finely powdered salt was treated with an aqueous solution of so much ammonia as to leave an approximately decinormal solution of the latter after the decomposition of the salt. The separated morphine was then removed by filtration, and washed with successive small quantities of a *N*/10-aqueous solution of ammonia. The filtrate and washings were freed from dissolved morphine by repeated extraction with their own volume of chloroform, and then polarimetrically examined. 2·6 Grams of morphine salt digested with a solution (8·4 c.c.) containing 0·114 gram of ammonia and treated in this manner gave a solution which was examined in the polarimeter with the following result:

$$l=2,\ c=7\cdot31,\ \alpha_D\ 5\cdot43^\circ,\ [M]_D\ 64\cdot6^\circ.$$

The salt racemises as regards its acid component very rapidly in alcoholic solution. It is therefore not possible to obtain the more soluble morphine *l*-acid salt from the mother liquor after the crystallisation of the less soluble *d*-acid salt. On concentration of the mother liquor, the crystals which separate still contain an excess of the latter salt. Also, the degree of separation of the two diastereoisomeric salts attained depends greatly on the exact conditions under which crystallisation takes place. Different crops of crystals examined in the manner described above gave ammonium salts of the following molecular rotations: $[M]_D$ 43°, 48°, 64·6°, 50°, 68°, 52°, 53·5°.

Silver d-*Oximino*cyclo*hexane*-4-*carboxylate*.—Finely powdered morphine salt (6 grams), which had been twice crystallised from alcohol, was treated with an aqueous solution (8·8 c.c.) containing 0·253 gram of ammonia. The separated morphine was removed in the manner already described, and the resulting solution, after having been polarimetrically examined:

$$l=2,\ c=16\cdot634,\ \alpha_D\ 9\cdot57^\circ,\ [M]_D\ 50\cdot1^\circ,$$

was treated with an aqueous solution of 2·55 grams of silver nitrate. The silver salt was collected, washed, and dried exactly as in the case of the silver salt of the *l*-acid. It weighed 2·38 grams, and was analysed with the following results:

0·3961 gave 0·4623 CO_2 and 0·1387 H_2O. C=31·83; H=3·89.
0·4968 ,, 21·75 c.c. N_2 (moist) at 14° and 759 mm. N=5·14.
0·4876 ,, 0·2652 AgCl. Ag=40·94.
$C_7H_{10}O_3NAg$ requires C=31·82; H=3·79; N=5·30;
Ag=40·90 per cent.

A portion of the same preparation (1·0019 grams), on treatment with an alkaline solution of sodium chloride as described in the case of the silver salt of the *l*-acid, gave a solution of dextrorotatory sodium salt, which was polarimetrically examined, with the following result:

$$l=2\ ;\ c=4\ 8523\ ;\ \alpha_D^{16}\ 2\cdot68^\circ\ ;\ [M]_D^{16}\ 49\cdot4^\circ.$$

Dextrorotatory silver salt of higher activity was subsequently obtained from a solution of ammonium salt of molecular rotation $[M]_D$ 64·6° ($c=7\cdot31$) made from a preparation of morphine salt (2·6 grams), which had been four times recrystallised from alcohol.

On treatment with silver nitrate, this gave 0·917 gram of silver salt, 0·6151 gram of which was converted into sodium salt in the manner described. The rotatory power of the resulting solution was as follows:

$$l=2,\ c=2{\cdot}979,\ \alpha_D\ 2{\cdot}48^\circ,\ [M]_D\ 74{\cdot}5^\circ.$$

Reducing Power of the Optically Active Sodium Salt.—For reasons given in the introduction (p. 1870), it appeared desirable to compare the reducing power of an active solution of the sodium salt of the oximino-acid towards Fehling's solution with that of β-phenylhydroxylamine on the one hand and that of acetoxime on the other.

1·62 Grams of quinine *l*-acid salt were treated with a solution (15 c.c.) of 0·2 gram of sodium hydroxide, and the separated quinine was removed by extraction with chloroform. For comparison with the solution of the sodium salt of the *l*-oximino-acid in *N*/10-sodium hydroxide thus obtained, solutions of equimolecular quantities of phenylhydroxylamine (0·37 gram) and of acetoxime (0·246 gram) in 15 c.c. of *N*/10-sodium hydroxide were prepared. The three solutions were respectively added at 20° to three quantities of Fehling's solution, each containing 1 gram of crystallised copper sulphate (1·2 mols.), 5 grams of Rochelle salt, 1·5 grams of sodium hydroxide, and 60 grams of water. The solution to which the phenylhydroxylamine had been added was, of course, completely reduced in a few seconds. The other two were kept well stoppered for twenty-four hours in a thermostat at 20°, and the small quantities of cuprous oxide which had been precipitated in each were collected and their respective amounts determined:

Precipitated by acetoxime: 0·013 gram Cu_2O; 0·065 atom Cu.

Precipitated by sodium salt of oximino-acid: 0·0316 gram Cu_2O; 0·132 atom Cu.

The reducing power of the sodium salt of the oximino-acid in alkaline solution is therefore, as was to be expected, of the same order of magnitude as that of acetoxime, and of an altogether different order from that of phenylhydroxylamine. There is therefore no reason to suppose that the hydroxylamine residue contained in these optically active salts possesses a constitution different from that usually assigned to it in the ketoximes.

The Racemisation Phenomena.

The Sodium Salt.—A solution of lævorotatory sodium salt free from excess of alkali was prepared by digesting active silver salt with a slight excess of an aqueous solution of sodium chloride. 2·40 Grams of quinine *l*-acid salt (giving sodium salt of molecular rotation $[M]_D$ −76·3°, $c=0·633$) were converted into ammonium salt in the manner already described, and the weakly ammoniacal solution of the ammonium salt thus obtained was treated with an aqueous solution of silver nitrate (0·935 gram). The precipitated silver salt, after having been carefully washed free from ammonia, was digested while still moist with an aqueous solution (20 c.c.) of 0·292 gram of sodium chloride. After thirty seconds, the solution of sodium salt thus obtained (which would be approximately 0·2-normal, and would also contain the slight excess of sodium chloride used) was filtered as rapidly as possible from silver chloride and examined in a 2-dcm. tube. The rotation was seen to diminish, the diminution taking place, as is shown in the accompanying table, in accordance with the unimolecular formula. The temperature was 20·4°:

t (mins.).	Rotation.	$1/t \log a/(a-x)$.
0·0	−1·44°	—
2·75	1·34	0·011
5·85	1·22	0·012
10·40	1·08	0·012
15·0	0·94	0·012
20·3	0·80	0·013
25·7	0·67	0·013
35·9	0·51	0·013
47·3	0·36	0·013

Taking 0·0125 as the value of the constant, the period of half-change is twenty-four minutes.

Sodium Salt in Presence of Sodium Hydroxide.—The solution on which the observations were made was prepared in the following manner. 2·50 Grams of quinine *l*-acid salt were treated with an aqueous solution (10 c.c.) of 0·246 gram of sodium hydroxide. The liberated quinine was removed with chloroform, and the separating funnel washed with small quantities of $N/10$-sodium hydroxide solution. The resulting solution was placed in a 2-dcm. tube, which was kept between the observations in a thermostat at 20°. The rotation was found to be continually decreasing, again in accordance with the unimolecular formulæ, but very much more slowly than in the previous experiment.

t (hours.).	Rotation.	$1/t \log a/(a-x)$.
0·0	−3·42°	—
1·96	3·20	0·0147
3·95	3·00	0·0144
5·66	2·85	0·0140
7·75	2·66	0·0141
9·88	2·49	0·0140
21·62	1·71	0·0139
24·24	1·57	0·0139
26·75	1·44	0·0140
29·75	1·33	0·0138
46·23	0·79	0·0138

Taking the value of the constant to be 0·0139, the time of half-change is 21·7 hours—fifty-four times as great as that for the sodium salt in neutral solution. The concentration of the sodium hydroxide was determined after the polarimetric observations were finished by titrating 10 c.c. of the solution with *N*/10-sulphuric acid, using phenolphthalein as indicator. It was thus found to be 0·098-normal. The concentration of the sodium salt, calculated from the quantity of quinine salt taken, was 0·32-*N*.

Ammonium Salt.—An approximately 0·2-*N*-solution of lævorotatory ammonium salt was prepared by a method exactly analogous to that employed in the case of the sodium salt. The same quantity of quinine *l*-acid salt (2·4 grams) was converted into ammonium salt (the molecular rotation of which was $[M]_D$ −72·8°, $c = 5·674$) and the silver salt obtained from it by precipitation with silver nitrate was digested with a solution of 0·267 gram of ammonium chloride in 20 c.c. of water. The resulting solution of lævorotatory ammonium salt was observed as rapidly as possible in a 2-dcm. tube, the temperature being 18·5°. The rate of diminution of the rotation was approximately twice as great as in the corresponding solution of sodium salt:

t (mins.).	Rotation.	$1/t \log a/(a-x)$.
0·0	−1·72°	—
1·87	1·56	0·023
3·43	1·43	0·023
4·73	1·34	0·023
6·47	1·23	0·023
7·62	1·15	0·023
9·13	1·08	0·022
10·58	0·99	0·023
12·37	0·90	0·023
14·55	0·77	0·024
17·35	0·68	0·023
21·83	0·55	0·023
25·77	0·42	0·024
39·65	0·19	0·024

The constant 0·023 corresponds with a period of half-change of 13·1 minutes.

Ammonium Salt in presence of Ammonium Hydroxide.—These observations were made on a dextrorotatory solution prepared from 3·0 grams of morphine *d*-acid salt by digestion with 8·18 c.c. of a normal solution of ammonia, the morphine being removed in the manner described by filtration and extraction of the filtrate and washings with chloroform. The final volume was 14·5 c.c. The excess of ammonia present could not readily be determined, but the above quantities were adjusted so as to give an approximately *N*/10-solution. The concentration of the ammonium salt calculated from the quantity of morphine salt used was 0·47-*N*. The solution was placed in a 2-dcm. tube, and kept between the observations in a thermostat at 20°:

t (hours.).	Rotation.	$1/t \log a/(a-x)$.
0·0	5·00°	—
1·66	4·36	0·0358
2·47	4·08	0·0358
3·57	3·73	0·0356
4·73	3·39	0 0357
5·83	3·12	0·0351
6·72	2·89	0·0354
8·30	2·54	0 0354

The mean value of the constant (0·0355) corresponds with a period of half-change of 8·48 hours. The rate of racemisation of the ammonium salt is therefore thirty-nine times less in the presence of this excess of ammonium hydroxide than under the conditions of the previously described experiment.

Mutarotation of the Morphine d-*Acid Salt in Aqueous Solution.*—The morphine salt is readily soluble in cold water. If the aqueous solution is polarimetrically examined as soon as possible after its preparation, its lævorotatory power is found to be quickly increasing. The change is, however, rapidly completed (practically), and after about seven minutes no further alteration in the rotation is to be detected. If the solution is now decomposed by the addition of a slight excess of ammonia and the morphine removed, the resulting ammonium salt is quite inactive. The mutarotation is therefore due to the racemisation of the acid component of the salt.

One gram of finely powdered morphine salt, giving ammonium salt of molecular rotation $[M]_D$ 51·7° ($c = 0·844$) was added to 20 c.c. of water. As soon as most of the salt had dissolved, the solution was filtered, and its rotatory power observed in a 2-dcm. tube, the first observation being completed 1·75 minutes after first wetting the salt. The temperature was 26·5°:

t (mins.).	Rotation.	Δ.	Δ (calc.).
0·0	−7·13°	0·54°	—
1·03	7·41	0·26	0·27°
1·91	7·50	0·17	0·15
2·72	7·58	0 09	0 09
4·77	7·66	0·01	0 02
6 70	7·66	0·01	0 01
12·13	7·67	0·00	0·00
∞	7·67	—	—

Under Δ are given the differences between the rotations observed, and the value finally attained. The numbers in the last column are calculated by means of the unimolecular formula, k being taken as 0·29, corresponding with a period of half-change of 1·04 minutes. They agree with the observed differences within the limits of experimental error.

The Mutarotation of the Quinine Salts of the d- *and* l-*Acids.*—The quinine salts are not sufficiently soluble in water to allow of satisfactory observations being made in that solvent, and although they possess a high solubility in alcohol, when brought into contact with it they form gummy masses, which pass comparatively slowly into solution. In the case of each salt, therefore, 0·8 gram was first finely ground up with 6 c.c. of ethyl acetate, and 12—14 c.c. of absolute alcohol then added to the mixture, when solution took place very rapidly. The solutions thus obtained were filtered and observed in a 2-dcm. tube, the temperature being 20° in each case. The quinine *l*-acid salt used was a sample which gave sodium salt of molecular rotation $[M]_D -67{\cdot}3°$ ($c=0{\cdot}731$), the quinine *d*-acid salt gave ammonium salt of molecular rotation $[M]_D$ $40{\cdot}4°$ ($c=0{\cdot}947$).

Quinine d-*Oximinocyclohexane-4-carboxylate.*

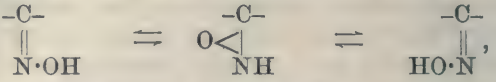
t (mins.).	Rotation.	Δ.	Δ (calc.).
0·0	−9·16°	0·44°	0·46°
3·0	9·35	0·25	0·24
3·7	9·38	0·22	0·20
5·0	9·47	0·13	0·15
9·6	9·56	0·04	0·05
15·3	9·60	0·00	0·01
20·4	9·59	0·01	0·00
∞	9·60	—	—

Quinine l-*Oximinocyclohexane-4 carboxylate.*

t (mins.).	Rotation.	Δ.	Δ (calc.).
0·0	−11·70°	0·89°	—
2·1	11·37	0·56	0·55
3·1	11·23	0·42	0·44
5·2	11·08	0·27	0·27
6·4	10·98	0·17	0·20
7·9	10·96	0·15	0·14
9·8	10·92	0·11	0·09
12·5	10·87	0·06	0·05
21·7	10·82	0·01	0·01
∞	10·81	—	—

The lævorotation was seen to increase in the case of the quinine *d*-acid salt and to diminish in that of the quinine *l*-acid salt, the rate of change agreeing (within the probable limits of error of the single rapidly made observations) with that calculated from the unimolecular formula when the velocity constant is taken as 0·1 in each case, corresponding with a period of half-change of three minutes.

The character of the differences among the velocity constants observed in these experiments might suggest that the rate of racemisation of the salts was connected with their degree of hydrolysis in the different solutions investigated—that the non-hydrolysed portion of the salt racemises very slowly, and that the observed loss of activity is mainly brought about through the rapidly racemising free acid present in larger or smaller proportion according to the degree of hydrolysis. It would appear, however, that this simple hypothesis is inadequate, for whereas the rates of racemisation in the aqueous solutions of the sodium and ammonium salts investigated were found to be approximately in the ratio of 2 to 1, the relative proportions of free acid present in the two solutions, calculated from the dissociation constants of water and ammonia, were of the order of 100 to 1. Other factors must therefore probably be taken into account. For example, it is conceivable that the interconversion of the *d*- and *l*-modifications should take place through an iso-oximino-form:



$$\begin{array}{c}-\text{C}-\\ \| \\ \text{N}\cdot\text{OH}\end{array} \rightleftharpoons \text{O}{<}\begin{array}{c}-\text{C}-\\ | \\ \text{NH}\end{array} \rightleftharpoons \begin{array}{c}-\text{C}-\\ \| \\ \text{HO}\cdot\text{N}\end{array},$$

and that the effects which acids and alkalis produce on the rate of racemisation are brought about through their influence on the relative proportion of the latter form present in the solutions.

The authors propose to extend this investigation to other compounds containing doubly-linked tervalent nitrogen. In conclusion, they desire to express their indebtedness to the Research Fund Committee of the Chemical Society for a grant by which the expenses of this work have been largely defrayed.

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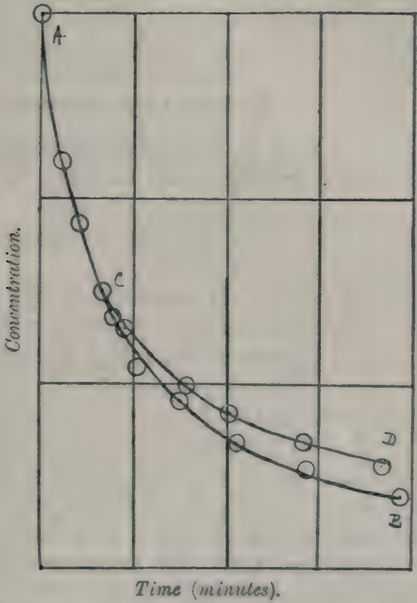
CC.—*Kinetics of the Reaction between Silver Salts and Aliphatic Iodides.*

By Frederick George Donnan and Harold Edward Potts.

The reaction between silver nitrate and alkyl iodides in alcoholic and aqueous-alcoholic solutions has been studied from a kinetic point of view by Burke and Donnan (Trans., 1904, **85**, 555; *Zeitsch. physikal. Chem.*, 1909, **69**, 148). The conclusion was drawn that the reaction is pseudo-bimolecular in type, and that the course of the reaction is affected by an accelerating influence due to some product. The following experiments have been carried out with the purpose of throwing further light on the mechanism of the reaction. They deal with the reaction between ethyl iodide and silver salts other than the nitrate, the reaction between ethyl iodide and silver nitrate in a non-hydroxylic solvent (acetonitrile), and the reaction between silver nitrate and aliphatic polyiodides (in alcoholic solution).

The diminution in the velocity-coefficient with decreasing initial concentration in the reaction between ethyl iodide and silver nitrate in alcohol led Burke and Donnan to the conclusion that the velocity of the reaction is accelerated by some product (although it was shown that this product could not be ethyl nitrate, ether, or nitric acid). This fact is clearly shown by Fig. 1, in which the ordinates represent concentrations, and the abscissæ times. Curve *AB* represents the time-concentration curve for the reaction $N/40\text{-AgNO}_3 + N/40\text{-C}_2\text{H}_5\text{I}$ in dry alcohol, whilst *CD* is the corresponding curve for the reaction $N/80\text{-AgNO}_3 + N/80\text{-C}_2\text{H}_5\text{I}$ in the same solvent at the same temperature (Burke and Donnan, Trans., *loc. cit.*). In the figure, the time-zero for the second curve (*CD*) has been shifted to the time-point (abscissa) when the primary reactants corresponding with the first curve (*AB*) have fallen to a concentration of $N/80$. The non-coincidence of these curves and the greater steepness of *AB* show that the velocity of the reaction is accelerated by some product. The reaction is therefore from a kinetic point of view a "disturbed" one, and the fair degree of constancy of the velocity-coefficient of the simple bimolecular equation in any particular experiment can only be explained as due to some compensating effect.

FIG. 1.



A special experiment made to test this conclusion showed that in the filtered reaction fluid resulting from a previous reaction, and containing no silver salt or alkyl iodide, the reaction proceeded (on addition of fresh portions of the reactants) more rapidly than in the pure solvent, the acceleration observed being in the ratio calculable from the results of Burke and Donnan.

In view of this disturbance, the constancy of the velocity-coefficient of the "bimolecular" equation in any given case does not prove that the reaction is really one of the second order. In the absence of the accelerating effect referred to, it is clear that the velocity-coefficient calculated from the simple bimolecular equation, $-dc/dt = kc^2$, would fall during the course of the reaction. This shows that the exponent of c, that is, the order of the reaction, must be higher than 2. In fact, although the Noyes-van't Hoff method is not strictly applicable to a case such as the present where the products exercise an accelerating influence, if we apply it to only a 10 per cent. change in the $N/40$- and $N/80$-reaction curves shown in Fig. 1, the value $n = 2{\cdot}8$ is obtained for the exponent of c. It is possible that this result may be explained by considering the varying electrolytic dissociation of the silver nitrate, as described on p. 1889 (results with silver lactate in aqueous alcohol).

Units and Method of Measurement.

The "dry" alcohol used in the following experiments was prepared by long-continued boiling of the ordinary "absolute" alcohol with excess of freshly prepared calcium oxide. The alcohol so obtained was then freed from reducing substances by distillation from a small quantity of silver nitrate.

The reaction-velocities were all measured at 25°, and the amount of silver salt in solution estimated by titration with thiocyanate solution. The numbers given in the tables are expressed in terms of the following units. Unit of volume = 1 c.c.; unit of mass = fraction of a molecule contained in 1 c.c. of a $N/100$-solution. Thus, the concentration of a $N/10$-solution = 10. The velocity-coefficients calculated with these units are six times greater than those calculated with the units employed by Burke and Donnan in their first paper. The unit of time employed is one minute. The values of k, the velocity-coefficient, have been calculated from the ordinary bimolecular equation except when otherwise stated.

The reaction fluids were previously warmed in separate vessels in the thermostat, and at a given time-point rapidly mixed. Definite equal volumes of the mixture were then quickly transferred by means of a previously warmed pipette into a series of small flasks placed in the thermostat.

Experiments with Silver Lactate in Aqueous Alcohol.

It has been shown in the case of silver nitrate that, although the velocity-coefficient of the bimolecular equation remains fairly constant in any given reaction, the velocity of the reaction is undoubtedly increased by some reaction product.

Experiments were therefore made with another silver salt in order to see if this peculiar behaviour could be associated with the presence of the NO_3-group. Owing to the difficulty of getting silver salts sufficiently soluble in dry alcohol, the experiments were made with silver lactate in a composite solvent, obtained by mixing 40 volumes of water with 60 volumes of dry alcohol. It has been shown by Burke and Donnan that in a solvent of this composition the behaviour of silver nitrate and ethyl iodide resembles that in dry alcohol.

TABLE I.

Silver lactate, $3N/200 \times 0·95$; ethyl iodide, $3N/200$.

t ……	0	4·5	9·5	14·5	19·5	33	39·5	68·5
c_{Ag} …	1·43	1·285	1·16	1·07	1·00	0·835	0·785	0·615
k ……	—	0·0161	0·0160	0·0152	0·0145	0·0141	0·0136	0·0126

It will be observed that the bimolecular velocity-coefficient falls steadily during the course of the reaction.

Determinations of the amount of free acid produced during the reaction were made, the results of which are shown in the following table.

TABLE II.

t.	c_{acid}.	c_{Ag}.	$\frac{\text{Acid produced}}{\text{Silver used up}} \times 100$.
0	0·0	1·43	—
26	0·345	0·95	70
30	0·365	0·89	67
34	0·39	0·85	66
2 weeks	0·97	$<0·01$	70

The ratio of free acid produced to silver salt used up in the reaction remains constant. It is noteworthy that this ratio is practically the same as that observed by Burke and Donnan in the case of the reaction between silver nitrate and ethyl iodide in dry alcohol, although in this case the acid is different. The following two tables contain reaction-velocity measurements made with another sample of silver lactate at two different initial concentrations. The values of k are here calculated from point to point, and not from the beginning of the reaction to each time-point as in the previous table.

TABLE III.

Silver lactate, $3N/100 \times 0·96$; ethyl iodide, $3N/100$.

t ………	0	7	11	16	20	30	40
c_{Ag} ……	2·89	1·76	1·525	1·31	1·21	1·00	0·88
k ………	—	0·0302	0·0209	0·0200	0·0147	0·0157	0·0121

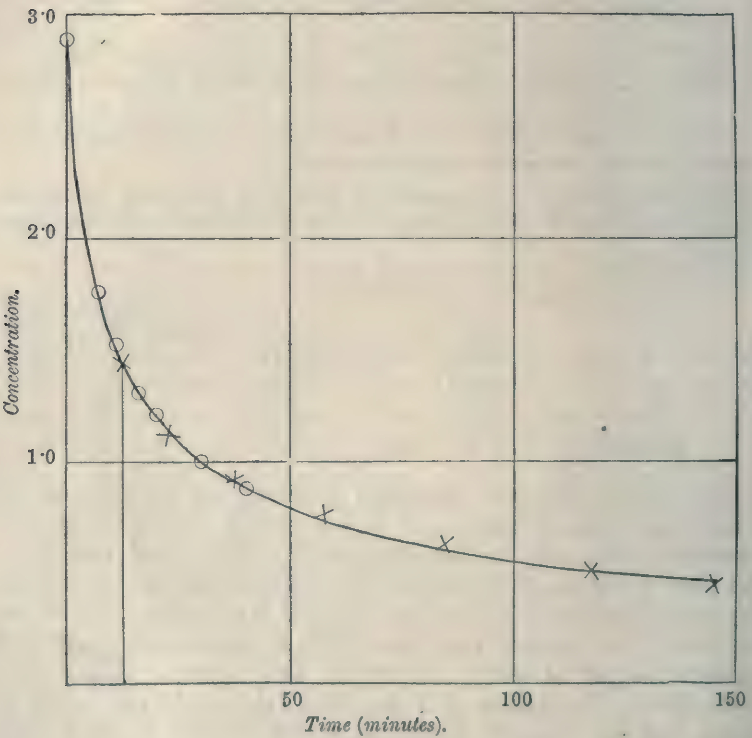
TABLE IV.

Silver lactate, $3N/200 \times 0{\cdot}96$; ethyl iodide, $3N/200$.

t	0	10	25	45	72	105	133	160
c_{Ag} ...	1·445	1·118	0·917	0·765	0·627	0·508	0·442	0·39
k	—	0·0205	0·0120	0·0100	0·0099	0·0103	0·0095	0·0098

If these two sets of times and concentrations are plotted, and the time-zero for the $3N/200$-reaction made to coincide with the time-point where the primary reactants of the $3N/100$-reaction have fallen to $3N/200$, as shown in Fig. 2, it will be seen that the two sets of points lie on the same continuous curve. This is in striking contrast to the case previously discussed (reaction between silver nitrate and ethyl iodide), and shows that in the present case the previously observed acceleration due to the products is absent.

FIG. 2.



It seems to be pretty certain therefore that in the case of silver nitrate the apparent constancy of the bimolecular reaction-coefficient is due to a compensating effect caused by the acceleration referred to. This is well shown by the following table, which contains the results of some further measurements of this reaction in the composite solvent employed above.

TABLE V.

Silver nitrate, $3N/100$; ethyl iodide, $3N/100$.

t	0	6	19	49	90	124	164
c_{Ag}	3·00	2·48	1·843	1·125	0·703	0·528	0·41
k	—	0·0117	0·0108	0·0116	0·0131	0·0136	0·0134

Here one observes a fair constancy of k, with, however, a tendency to increase towards the latter part of the reaction. A similar tendency is observable in some of the results previously given by Burke and Donnan (*loc. cit.*).

The practically constant ratio of lactic acid produced to silver lactate used up (66 to 70 per cent.) shows, as in the case of silver nitrate, that there must be at least two simultaneous reactions, in one of which the free acid is formed (Wegscheider's criterion).

Denoting the negative ion of the silver salt by A, we may represent these two reactions thus:

A . . . . . . $AgA + EtI \longrightarrow AgI + EtA.$

B . . . $AgA + EtI + EtOH \longrightarrow AgI + Et_2O + HA.$

In the case of aqueous solvents, there will also occur the reaction:

C . . $AgA + EtI + H{\cdot}OH \longrightarrow AgI + EtOH + HA.$

In the case of alcoholic or aqueous-alcoholic solvents, the reaction B (or $B+C$) is the main one, as only about 30 per cent. of the "theoretical" amount of the ester EtA is produced.

In order to explain this "abnormal" production of acid, Wegscheider and Fränkel (*Sitzungsber. Wien. Akad.*, 1907, **116**, Abt. IIb) have proposed the following hypothesis. They suppose that the essential cause of the reaction is the affinity of the silver and halogen atoms, and that this leads to a series of not sharply distinguishable intermediate stages in which there occurs a spatial approximation of the silver and halogen atoms. These may be roughly formulated as follows:

$$C_2H_5-I\ .\ .\ .\ .\ Ag-NO_3.$$

As a result of this, the "affinity" between C_2H_5 and I on the one hand, and Ag and NO_3 on the other is weakened, so that the above system may rearrange itself into the definite end-products AgI and $C_2H_5{\cdot}NO_3$, or may react with a molecule of the solvent to give (in the case of ethyl alcohol) the end-products AgI, $(C_2H_5)_2O$, and HNO_3.

It would seem difficult to distinguish between this hypothesis and what is usually understood by the assumption that a transient intermediate compound between the silver salt and the alkyl iodide is the first stage in the reaction. Moreover, Wegscheider's hypothesis does not lend itself to analytical treatment in the present condition of chemical science, so that it is impossible to apply to it any exact experimental test. We shall content ourselves therefore with examining the consequences of more definite hypotheses. In the first place, let us suppose that the velocity of the reaction is controlled by a direct interaction between one molecule of undissociated silver salt and one molecule of alkyl iodide. Considering only equivalent concentrations, and calling α the degree of dissociation of the silver salt, this leads to the equation:

$$-dc/dt = k(1-\alpha)c^2.$$

As α will increase, and therefore $1-\alpha$ decrease, with the progress of the reaction, the coefficient $k(1-\alpha)$ of the simple bimolecular equation will diminish as the reaction progresses. This is exactly what the experimental results show in the case where the reaction is not disturbed by the products. Let us now make the further assumption that the simple law of mass-action holds for the equilibrium between the undissociated silver salt and its ions. This leads to the equation $K(1-\alpha)=\alpha^2 c$, which, combined with the previous one, gives:

$$-dc/dt = k'\alpha^2 c^3.$$

Now, as α increases with the dilution, we should expect the coefficient $k'\alpha^2$ of the "termolecular" equation to increase with the progress of the reaction, but as, at the dilutions employed, α will not differ very far from unity, it is obvious that the increase of $k^1\alpha^2$ will be considerably smaller than the decrease of $k(1-\alpha)$.

The following table contains the values of k_3 corresponding to the equation $-dc/dt = k_3c^3$, as calculated from the curve given in Fig. 2.

The values of k_3 are calculated from point to point.

TABLE VI.

t	0	4·2	11·1	30·1	48·5	84·7	119·0
c	2·89	2·0	1·5	1·0	0·8	0·6	0·5
k_3	—	0·0298	0·0281	0·0292	0·0306	0·0336	0·0356

The coefficient of the simple bimolecular equation falls from 0·030 to 0·010 over the same range of concentration. The constancy of k_3 is surprising, and, indeed, even greater than could have been expected on the above hypothesis. This will be made clear by the following table:

α	0·7	0·8	0·9
α^2	0·49	0·64	0·81
$1-\alpha$	0·30	0·20	0·10

This table shows that if $(1-\alpha)$ falls in the ratio of 3 to 1, α^2 will increase by more than 50 per cent. Now, whilst the fall of the bimolecular velocity-coefficient is in reality in the ratio 3 : 1, the corresponding increase in the termolecular velocity-coefficient is only about 20 per cent. Too much stress need not be laid on this discrepancy, as the assumption that the simple law of mass-action holds for the electrolytic dissociation of the silver salt may be only a very rough approximation.

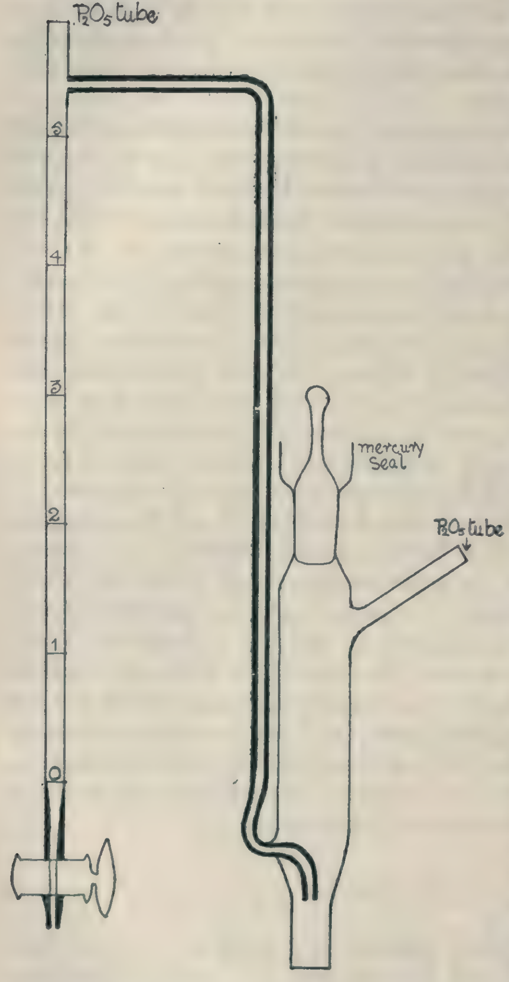
It is necessary also to remark here that if the simple law of mass-action be assumed, the equation $-dc/dt = k'\alpha^2 c^3$ can be equally well reconciled with the view that only the ions $Ag^{\cdot}$ and NO_3' react with the alkyl iodide. The results appear to show, however, that the reaction velocities due to undissociated silver nitrate on the one hand, and the ions $Ag^{\cdot}$ and NO_3' on the other, must be very different, so that the main effect must be due to either one or the other. Experiments carried out in alcohol as solvent have shown (Burke and Donnan, *Zeitsch. physikal. Chem.*, *loc. cit.*) that highly dissociated nitrates, such as ammonium nitrate, considerably increase the velocity of the reaction between silver nitrate and ethyl iodide. This seems to indicate that it is the undissociated silver nitrate molecules which are effective (at all events, in alcoholic solution).

Concerning the question of the formation of an intermediate compound, the experimental results are not decisive. If, as seems possible from the above, it is the undissociated silver salt which reacts, then it is a plausible hypothesis to assume that the velocity of the whole reaction is determined by the rate of formation of an intermediate compound between the silver salt and the alkyl iodide, this intermediate compound then rapidly changing to alkyl ester and silver iodide on the one hand, and, on the other, reacting with a molecule of solvent to form silver iodide, free acid, and an ether (or alcohol). There is, however, no experimental evidence which would enable one to test this hypothesis.

Experiments with Silver Nitrate in Acetonitrile.

The foregoing experiments, together with those of Nef (*Annalen*, 1899, **309**, 126), Burke and Donnan (*loc. cit.*), and Wegscheider and Fränkel (*loc. cit.*), have shown that when a silver salt reacts with an alkyl iodide in a solvent which contains the hydroxyl group, free acid is one of the main products. It was decided therefore to carry out some experiments in a non-hydroxylic solvent in order to examine the kinetics of the reaction when no free acid can be formed. As a few preliminary experiments showed that the reaction between silver nitrate and ethyl iodide proceeds with convenient speed in acetonitrile, and that the precipitate produced consists of silver iodide, a quantity of this solvent was shaken with phosphoric oxide, and then distilled from this reagent into a bottle provided with a phosphoric oxide guard-tube and mercury-sealed outlet-tube. The velocity of the reaction was measured in the apparatus shown in Fig. 3, the reaction-vessel being immersed in the thermostat. Twenty-five c.c. of the dry acetonitrile, containing a weighed quantity of silver nitrate, were introduced into the reaction vessel, then a weighed quantity of ethyl iodide (contained in a small stoppered tube) dropped in, the mercury-sealed stopper of the reaction-vessel replaced, and the contents thoroughly mixed by blowing in a current of dry air. At definite intervals, portions of the reaction-liquid were blown over into the burette, rapidly measured off, and titrated.

Fig. 3.



In the following tables, *k* is the velocity-coefficient of the simple bimolecular equation:

TABLE VII.

Silver nitrate, *N*/10; ethyl iodide, *N*/10.

t ……	0	15	36	66	88	115
c_{Ag} …	10·00	7·94	6·27	4·95	4·37	3·88
k ……	—	0·00173	0·00164	0·00155	0·00146	0·00137

k (mean) = 0·00155.

TABLE VIII.

Silver nitrate, *N*/20; ethyl iodide, *N*/20.

t	0	15·5	41	84	139	196	244
c_{Ag}	5·00	4·68	4·09	3·32	2·87	2·47	2·20
k	—	0·00090	0·00107	0·00120	0·00107	0·00105	0·00105

k (mean) = 0·00105.

TABLE IX.

Silver nitrate, *N*/40; ethyl iodide, *N*/40.

t	0	91	248	349
c_{Ag}	2·50	2·11	1·66	1·47
k	—	0·00081	0·00081	0·00081

k (mean) = 0·00081.

In these experiments the reaction-liquid at the end of the reaction was found to contain a small quantity of acid, but this was traced to the solvent, which was found to contain a small quantity of phosphoric acid sufficient to explain the acidity of the reaction-fluid. To obviate this, the acetonitrile, which had been previously dried by phosphoric oxide as described, was treated with freshly ignited lime and redistilled. The following experiment was carried out with the now neutral distillate:

TABLE X.

Silver nitrate, *N*/20; ethyl iodide, *N*/20.

t	0	98	130	157	166
c_{Ag}	5·00	3·33	2·95	2·73	2·73
k	—	0·00102	0·00106	0·00106	0·00100

k (mean) = 0·00104.

This value of *k* agrees very well with that previously found. It was noticed, however, that at the end of the experiment the reaction-fluid contained about the same (small) quantity of free acid as in the previous experiments. Probably the acetonitrile, after treatment with phosphoric oxide, contained a little ethyl phosphate (due to traces of alcohol), and this on distillation from lime regenerated the alcohol, which afterwards reacted to form free acid.

The above experiments prove that whilst the reaction proceeds normally (that is, without production of free acid) in acetonitrile as solvent, the reaction-kinetics closely resemble those obtained with alcohol as solvent. The simple bimolecular velocity-equation holds good for each experiment (although in the case of the *N*/10-reaction there is a decided drop), but the velocity-coefficient varies with the initial concentrations of the reactants. It is clear that the peculiar kinetic behaviour observed in hydroxylic solvents has nothing to do with the acid formation. As explained previously, this behaviour is probably to be accounted for by the varying dissociation of the silver salt, and, in the case of the nitrate, by the formation of some product which acts as an accelerator.

If time–concentration curves for the experiments with various initial concentrations be plotted as described on p. 1883, it will be found that in the case of acetonitrile as solvent the various curves so obtained cannot be made to superimpose, although the divergence is not nearly so marked as in the case of alcohol as solvent. This would seem to show that the accelerating effect referred to above is much smaller in the experiments with silver nitrate in acetonitrile.

Experiments with Iodoform in Alcoholic Solution.

Preliminary experiments showed that in dry ethyl alcohol at 25°, silver nitrate and iodoform (both $N/30$) react with convenient speed, the reaction occurring in the stoicheiometric ratio $3AgNO_3 : CHI_3$, and the precipitate produced being silver iodide. During the reaction free nitric acid is produced, and this slowly liberates iodine from iodoform, but if the experiment does not last more than a few hours, this secondary reaction may be neglected. The following tables contain the results of the velocity-measurements (k = coefficient of simple bimolecular equation):

TABLE XI.

$N/25$-$AgNO_3$; $N/25$-$(CHI_3/3)$.

t ……	0	30	45	60	120	210
c_{Ag} …	3·765	3·255	3·055	2·825	2·34	1·74
k ……	—	0·00136	0·00136	0·00146	0·00135	0·00147

Mean = 0·00140.

TABLE XII.

$N/30$-$AgNO_3$; $N/30$-$(CHI_3/3)$ (temp. = 25·2°).

t ……	0	52	70	82	92	116	155	173
c_{Ag} …	3·185	2·595	2·55	2·47	2·445	2·29	2·06	1·965
k ……	—	0·00136	0·00111	0·00111	0·00103	0·00106	0·00110	0·00113

Mean = 0·00113.

TABLE XIII.

$N/40$-$AgNO_3$; $N/40$-$(CHI_3/3)$.

t ………	0	52	71	94	148	167
c_{Ag} ……	2·45	2·265	2·175	2·13	1·945	1·87
k ……	—	0·00066	0·00073	0·00065	0·00072	0·00076

Mean = 0·00070.

TABLE XIV.

$N/30\text{-}AgNO_3$; $N/40\text{-}(CHI_3/3)$.

t………	0	19·25	42·5	85	98	210	232	303
c_{Ag} …	3·33	3·185	3·015	2·725	2·675	2·185	2·035	2·015
k ……	—	0·00090	0·00098	0·00107	0·00103	0·00110	0·00122	0·00097

Mean = 0·00104.

TABLE XV.

$N/52\text{-}AgNO_3$; $N/40\text{-}(CHI_3/3)$.

t ………	0	28	109	142	180	231	257
c_{Ag} ……	1·93	1·835	1·645	1·54	1·495	1·375	1·345
k ………	—	0·00062	0·00064	0·00070	0·00063	0·00071	0·00063

Mean = 0·00065.

An experiment was tried with a solution of iodoform in alcohol which had been preserved in the dark for eleven days. This solution reacted with silver nitrate with the same speed as a fresh solution.

The following table summarises the results obtained with iodoform:

TABLE XVI.

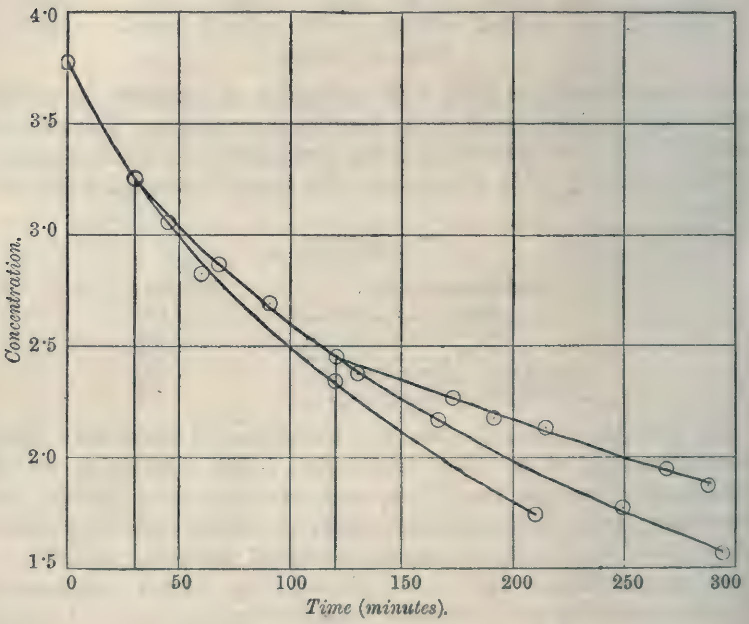
Initial concentration.	Value of $k \times 10^5$.
$N/25$ …………………	140
$N/30$ …………………	113
$N/40$ …………………	70
$N/30\text{-}AgNO_3$; $N/40\text{-}(CHI_3/3)$..	104
$N/40\text{-}AgNO_3$; $N/52\text{-}(CHI_3/3)$..	65

It will be observed that the behaviour of iodoform closely resembles that of an alkyl monoiodide. The reaction is pseudo-bimolecular in type, the velocity-coefficient increasing rapidly with increasing initial concentrations of the reactants, and being mainly dependent on the initial concentration of the silver nitrate. If time-concentration curves be plotted, the curves representing reactions starting at different initial concentrations cannot be superimposed, the reaction which starts at a lower initial concentration always proceeding markedly slower than a reaction which has reached the same concentration of the reactants from a higher initial concentration. As shown in Fig. 4, this divergence is greater than in the case of the reaction between silver nitrate and ethyl iodide in alcohol as solvent.

The constancy of the bimolecular velocity-coefficient in spite of such a great acceleration due to the products proves that in the absence of this disturbing effect the order of the reaction would be much higher than 2. Indeed, an application of the Noyes-van't Hoff method to the initial portions (10 per cent. change) of the various reaction-curves plotted above yields, for the order of the reaction, numbers the mean of which is about 3·8. It is probable therefore that the real order of the reaction is between 3 and 4, and nearer 4 than 3. With the data at hand, it is not possible to go further than this. In particular, it is not possible to decide whether the reaction proceeds in a series of successive stages, though the somewhat analogous case of the alkali hydrolysis of the triglycerides would render this view probable.

As in the case of the alkyl iodides, the reaction proceeds with formation of free acid. For the reaction starting at *N*/30-equivalent concentrations of silver nitrate and iodoform, the free nitric acid found at the completion of the reaction was equivalent to 85 per cent. of the original silver nitrate. This is a higher amount than that observed in the case of ethyl iodide.

FIG. 4.



The following experiment is a good example of a "rapid" reaction, in which one of the reactants is a carbon compound. If a small quantity of finely powdered silver nitrate be cautiously mixed with the equivalent amount of solid iodoform, a scratch or light blow is sufficient to set up a violent reaction, in which clouds of iodine vapour and oxides of nitrogen are evolved.

Experiments with Methylene Iodide and Carbon Tetraiodide in Alcoholic Solution.

The experiments recorded in the previous section show that iodoform reacts with silver nitrate in alcoholic solution at 25° about eight times more slowly than methyl iodide. A few experiments carried out with methylene iodide and silver nitrate in alcoholic solution showed that the velocity-coefficient is about one hundred times smaller than the corresponding coefficient for iodoform. In point of reactivity with silver nitrate, methylene iodide does not therefore occupy a position intermediate between methyl iodide and iodoform, but is characterised by a very great sluggishness.

Carbon tetraiodide was prepared by a modification of Gustavson's method, but it was found impossible to carry out any satisfactory measurements of its velocity of reaction with silver nitrate, as in alcoholic solution the tetraiodide loses iodine with comparative rapidity. Some special experiments on this point showed that in a solution containing 0·1 gram of tetraiodide in 20 c.c. of alcohol, 95 per cent. of the iodine of the tetraiodide is present as free iodine after sixteen hours.

On adding an alcoholic solution of silver nitrate to an alcoholic solution of carbon tetraiodide there is an immediate diminution in the amount of dissolved silver salt, due to interaction with the free iodine. After this, the concentration of the silver salt diminishes very slowly, so that the carbon tetraiodide itself does not react at all rapidly with silver nitrate in alcoholic solution.

In conclusion, the authors desire to express their best thanks to the Research Fund Committee of the Chemical Society for a grant which helped to defray the expenses of this investigation.

Note.—Since the completion of the above work, a paper has appeared by G. Senter (Trans., 1910, **97**, 346), in which this author finds that in the reaction between silver nitrate and methyl iodide in alcoholic solution, precipitated (or colloidal) silver iodide exerts a slight accelerating effect on the velocity of the reaction. It may be possible therefore that this is the product of the reaction which produces the accelerating effect discussed in the foregoing paper. It is somewhat difficult, however, to reconcile this view with the apparent absence of the accelerating action in the reaction between silver lactate and ethyl iodide in aqueous-alcoholic solution. The matter requires further investigation before this point can be definitely settled.

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CCI.—*Changes in Volume in the Formation of Dilute Solutions. Part II. Relationship between Change in Volume and Constitution.*

By HARRY MEDFORTH DAWSON.

IN Part I of this work (this vol., p. 1041) an account was given of the volume changes which occur in the formation of dilute solutions of iodine and naphthalene. From the fact that the sequence of the solvents, when arranged according to the magnitude of the volume changes, is quite different for the two dissolved substances, the conclusion was drawn that these changes in volume cannot, in general, be interpreted in terms of any property or properties of the pure solvents. This was shown to be the case whether it is assumed that the observed volume change is entirely due to a change in the volume of the dissolved substance, or whether the change is debited entirely to the solvent.

There can be no doubt that neither of these limiting views is correct, and according to Tammann (*Zeitsch. physikal. Chem.*, 1896, **21**, 529), the volume change Δv occurring in the formation of a solution must in general be represented by an equation of the form:

$$\Delta v = \Delta\phi_1 + \Delta\phi_2 + \Sigma\Delta\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

In this equation $\Delta\phi_1$ and $\Delta\phi_2$ represent respectively the alterations in volume experienced by the solute and the solvent when the pressures acting on these are changed from the values representing the internal pressures of the pure substances to the common internal pressure of the solution. The term $\Sigma\Delta\phi$ represents the further change in volume which is supposed to take place when the solvent and solute are then mixed together without any alteration in the value of the pressure to which the components of the system are subjected.

In justification of the term $\Sigma\Delta\phi$, Tammann cites the experimental measurements of Braun (*Ann. Physik*, 1888, [iii], **34**, 943), according to which the mixing of gases, even at atmospheric pressure, is accompanied by appreciable volume changes. The inference drawn by Tammann from these observations does not appear, however, to be very conclusive. In the first place, it should be noticed that in Braun's experiments, the different gases were allowed to mix without change in the manometrically measured pressure. For one and the same external pressure, the gases are, however, subjected to different internal pressures or total pressures, and this is more particularly so in the case of the more easily condensible gases, such as sulphur dioxide and carbon dioxide, which, when mixed with equal volumes of hydrogen or nitrogen, were found to give rise to relatively large changes of volume at atmospheric pressure. Furthermore, the internal pressure of the mixed gases will, in general, be different from the internal pressures of the unmixed gases, although the manometrically measured pressure retains the same value. Some idea of the magnitude of the volume changes, which may result from the operation of these internal pressure differences, is obtained if we consider the variation of the product pv at low pressures. According to measurements of Fuchs (Castell-Evans, *Physico-chemical Tables*, p. 450), the value of pv changes in the ratio 1 : 1·0251 for sulphur dioxide, 1 : 1·0063 for carbon dioxide, and 1 : 0·9988 for air when the pressure is reduced from 1000 to 250 mm. of mercury.

From the above considerations, it would appear that the deviations from the additive law of gas volumes observed by Braun are not directly applicable to the process of the mixing of liquids (or gases) under the conditions stipulated by Tammann.

We may now consider the admixture of two different liquids A_1 and A_2 a little more closely from the point of view of internal pressure, or rather from that of the molecular forces of attraction which give rise to this pressure. If the specific molecular attraction of the pure liquids is denoted by a_1 and a_2, and the corresponding attraction between the molecules of A_1 and A_2 by $a_{1\cdot2}$, and if the molecular volumes of the unmixed liquids are v_1 and v_2 and the volume of the mixture is $v_{1\cdot2}$, then the internal pressures of A_1, A_2, and (A_1+A_2) are given by a_1/v_1^2, a_2/v_2^2, and

$$(a_1/v_{1\cdot2}^2+a_2/v_{1\cdot2}^2+2a_{1\cdot2}/v_{1\cdot2}^2)$$

respectively. In the ideal process of mixing, from the consideration of which equation (1) is derived, the two internal pressures a_1/v_1^2 and a_2/v_2^2 are supposed to be reduced to the common value $(a_1+a_2+2a_{1\cdot2})/v_{1\cdot2}^2$ before the actual mixing is carried out. If these conditions are fulfilled, it is difficult to see on what grounds a change in volume corresponding with $\Sigma\Delta\phi$ is to be anticipated. In the author's opinion the conditions of the process are such as to preclude the possibility of such a volume change, and equation (1) reduces therefore to the simpler form:

$$\Delta v=\Delta\phi_1+\Delta\phi_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

In reference to the validity of this equation as an expression of the volume change which occurs in the mixing of two liquids, it should be noted that it is tacitly assumed that the mixing process is not accompanied by any change in the molecular complexity of either of the two liquids, that is to say, by association or dissociation phenomena, nor yet by any change in the nature of chemical combination between the two sets of molecules. Pairs of substances which satisfy these conditions may for convenience be referred to as "normal" substances, and the solutions obtained by mixing them as "normal" solutions.

As a consequence of the elimination of the term $\Sigma\Delta\phi$ from equation (1), the expression for the change in volume which occurs in the formation of a solution is greatly simplified. If the specific volumes of the two components (solute and solvent) in the pure liquid condition are denoted by ϕ_1^l and ϕ_2^l, and the true volumes of these components in the solution containing x parts of A_1 and $(1-x)$ parts of A_2 are represented by ϕ_1^s and ϕ_2^s, the change of volume in the formation of unit quantity of solution may be written:

$$\Delta v = x(\phi_1^l - \phi_1^s) + (1-x)(\phi_2^l - \phi_2^s) \quad . \quad . \quad . \quad . \quad (3).$$

If P_1 and P_2 are the internal pressures of the pure liquids, P_3 that of the solution, and if β_1 is the mean compressibility of A_1 (referred to unit quantity) between the pressure limits P_1 and P_3, and β_2 is the corresponding value of the compressibility of A_2 between P_2 and P_3, the above equation may be written in the form:

$$\Delta v = x\beta_1(P_1 - P_3) + (1-x)\beta_2(P_2 - P_3) \quad . \quad . \quad . \quad (4).$$

According to this equation, the change in volume is dependent on the proportions of the two substances in the solution and on their compressibilities between certain limits of pressure. Of these limiting pressures, P_3 is common to the two substances, and is a function of x, the value of which determines the composition of the solution. According to results obtained by von Biron (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 188) for pairs of liquids which appear to conform to the above definition of "normal" pairs, P_3 is a linear function of x, and its connexion with the internal pressures P_1 and P_2 of the pure liquids is given by $P_3 = xP_1 + (1-x)P_2$. If this result is accepted as a first approximation, substitution for P_3 in equation (4) leads to:

$$\Delta v = x(1-x)(P_1 - P_2)(\beta_1 - \beta_2) \quad . \quad . \quad . \quad . \quad . \quad (5).$$

In the case of a dilute solution in which one of the components (the solvent) is present in large excess, x may be neglected in comparison with unity, and equation (5) may then be written in the form:

$$\Delta v / x = (P_1 - P_2)(\beta_1 - \beta_2) \quad . \quad . \quad . \quad . \quad . \quad (6),$$

in which $\Delta v/x$ is the change in volume referred to unit quantity of the solute.

According to this, the volume change which accompanies the formation of dilute solutions of one and the same substance (P_1 = constant) in different solvents is dependent on the internal pressure P_2 of the solvent and on the compressibilities β_1 and β_2 of the solute and solvent respectively. The compressibilities are, of course, dependent on the pressure limits which are involved in a particular case, and in the absence of a sufficiency of data connecting pressure and compressibility it is not possible to subject equation (6) to a rigorous experimental examination. We may, however, inquire to what extent the relative magnitudes of the changes of volume observed in the formation of the dilute solutions investigated in the first part of this paper are in agreement with the requirements of this equation, according to which the change in volume is influenced by two independent factors, one of which may be referred to as the internal pressure factor, and the other as the compressibility factor. If now we compare solvents of approximately equal internal pressures, but considerably different compressibilities, then according to equation (6) we may expect to find a connexion between the relative volume changes and the compressibilities of the solvents. On the other hand, if solvents are compared which have approximately equal compressibilities and different internal pressures, it is to be anticipated that the volume changes will be related to the internal pressure values.

Such relationships may not, however, be apparent unless the conditions stipulated in connexion with equation (2) are fulfilled. The solutions must be "normal" in the sense already defined; that is to say, the formation of the solutions must not be accompanied by changes in the degree of complexity of the solute or solvent, and the solute must not enter into chemical combination with the solvent.

In the case of dilute solutions of iodine which will be specially discussed in this paper, molecular-weight determinations have shown that the first condition in regard to the solute is fulfilled quite generally. Whatever the nature of the solvent, dissolved iodine appears to be present in the form of diatomic molecules. Experiment furnishes no evidence in respect of the constancy of the degree of complexity of the solvent, but for dilute solutions it is safe to assume that this condition is generally satisfied by the different solvents. It is, however, an entirely different matter in regard to the absence of chemical combination.

Recent work relating to the cause of the differences in colour of iodine solutions appears to point to the conclusion that these differences are due to variations in the extent to which iodine is combined with the solvent. From these investigations, in reference to which attention may be called to a paper by Waentig (*Zeitsch. physikal. Chem.*, 1909, **68**, 513), it is probable that violet-coloured solutions of iodine are those which approximate more closely to what have been termed "normal" solutions than do the red and brown solutions. As the ability to transmit the more refrangible visible rays diminishes, the deviation from this "normal" type increases, and an increasing proportion of the dissolved iodine is chemically combined with the solvent.

The extent to which the formation of solvates may modify the volume changes which occur in the formation of solutions cannot be estimated in any particular case. It is very probable, however, that these complex molecules are formed with a diminution in volume the magnitude of which will depend on the specific nature of the solvent. This view is supported by the results of experiments in which iodine was dissolved in solvents containing soluble polyiodides. At the same time, some idea is obtained of the extent to which the chemical combination of the dissolved iodine may influence the observed volume changes.

Experiments were made with solutions of potassium iodide and iodine in nitrobenzene and in ethyl acetate. In these solutions the added iodine combines to a large extent with the dissolved substance or substances already present to form a higher polyiodide or polyiodides, and the difference between the "solution volumes" represents therefore the "molecular solution volume" of combined iodine as distinguished from that of free iodine, the corresponding values for which are appended for comparison in the table:

	Nitrobenzene.		Ethyl acetate.
"Solution volume" of $KI + 3I$	198·3 c.c.	$KI + 4I$	147·3 c.c.
,, ,, ,, $KI + 5I$	133·1 ,,	$KI + 61$	210·5 ,,
"Molar sol. vol." of combined iodine	65·2 ,,	combined iodine.	63·2 ,,
,, ,, ,, free iodine	67·2 ,,	free iodine	64·5 ,,

Since the polyiodide solutions in the case of both solvents are good conductors, and therefore ionised to a considerable extent, and since changes in the degree of ionisation are accompanied by appreciable changes in volume (compare Walden, *Zeitsch. physikal. Chem.*, 1907, **60**, 87), conductivity measurements were made before and after the addition of iodine to ensure that no changes in volume due to this factor were involved. From the values of the "molecular solution volume" of the free and combined iodine, it is evident that the combination of the iodine is accompanied by a contraction of 2 c.c. per gram-molecule in nitrobenzene solution, and of 1·3 c.c. in the solution in ethyl acetate. Volume changes of this order of magnitude may therefore be expected in the formation of so-called solvates.

If the change in volume resulting from the chemical combination is relatively small, the effect of the solvate formation may not be sufficient to modify appreciably the influence of those factors which otherwise determine the connexion between the total volume change and the nature of the solvent. On the other hand, if the change in volume due to solvate formation is relatively large, the influence of the internal pressure and the compressibility of the solvent on the observed change in volume may be completely overshadowed.

From equation (6) and the above considerations relating to solvate formation, it follows that, in general, the volume changes which occur when the same quantity of iodine is dissolved in different solvents to form dilute solutions are dependent on (1) the internal pressure of the solvent, (2) the compressibility of the solvent, and (3) the contraction which accompanies the chemical combination of a smaller or larger proportion of the iodine with the solvent.

Whatever the nature of the dissolved substance, these are the determining factors, and the only reason for the selection of iodine for consideration is the fact that more evidence in regard to its molecular condition in solution in different types of solvents has been obtained than in the case of any other single substance. The advantages attaching to the examination of a coloured substance, such as iodine, which is characterised by specific activity towards visible light rays, are not inconsiderable from the point of view of the general theory of solutions. Other specific properties, such as optical rotatory power, are of still greater value in connexion with quantitative measurements, and the importance of optical activity on the part of one of the components of a solution in connexion with the investigation of the nature of solutions has been rightly emphasised by Winther (*Zeitsch. physikal. Chem.*, 1907, **60**, 590, 641, 685).

From the experimental data for solutions of iodine and naphthalene recorded in Part I. (*loc. cit.*), the conclusion was drawn that the changes in volume associated with different solvents cannot in general be accounted for by reference to the internal pressures or other properties of the solvents. This conclusion is consistent with the result which is now obtained as a consequence of a closer examination of the factors which are operative in determining these volume changes. In view of the fact that the volume change is, in general, determined by three independent factors, it is not possible to subject the experimental results to any very detailed analyses. Certain relationships having an obvious connexion with the view developed in this paper may, however, be referred to.

When the fifteen solvents investigated are arranged according to the magnitude of the change in volume which occurs when iodine is dissolved in them, we obtain a series in which nitrobenzene is the first member, and ethyl ether the last. Per gram-molecule of iodine, the formation of a solution in nitrobenzene is accompanied by an expansion of 8·7 c.c., and in ethyl ether by a contraction of 8·0 c.c.* Of all the solvents examined, nitrobenzene is the least compressible, and ethyl ether is by far the most compressible, and since the internal pressures of the two liquids are not very different, the observed volume changes are obviously in accordance with what would be anticipated from equation (6). With naphthalene as dissolved substance, the relative volume changes in the case of these two solvents are quite similar, in that nitrobenzene, as the second member of the series of fifteen solvents, shows the next largest expansion, whilst ethyl ether gives rise to by far the largest contraction.

Carbon tetrachloride and carbon disulphide are two other solvents which may be compared. Both yield violet solutions, and the dissolved iodine is therefore probably present, for the most part, in the free condition; their compressibilities also appear to be approximately equal. In these circumstances a connexion between the volume changes and the internal pressures of the solvents may be expected. According to Walden and Traube, the internal pressure of carbon disulphide is about 50 per cent. greater than that of carbon tetrachloride, and in agreement with this it is found that the solution of one gram-molecule of iodine in carbon tetrachloride is accompanied by an expansion of 7·3 c.c., whereas the corresponding expansion for the solution in carbon disulphide is only 2·6 c.c. When the volume changes associated with the formation of solutions of naphthalene in these two solvents are compared, the relative positions are, however, reversed. For a gram-molecule of naphthalene, there is a contraction of 0·75 c.c. in carbon tetrachloride, and an expansion of 1·35 c.c. in carbon disulphide. In the case of naphthalene there is no evidence of the molecular condition of the dissolved substance apart from its degree of complexity, and the relative volume changes lead to the supposition that the naphthalene enters into combination with carbon tetrachloride to form addition compounds to a greater extent than it does in the case of carbon disulphide.

In reference to the view that brown solutions of iodine contain a considerable proportion of the iodine in combination with the solvent, the fact may be mentioned that all solutions which contain combined iodine in the form of polyiodides of the alkali and alkaline earth metals and of hydrogen appear to have a brown colour. In certain cases, as, for example, the brown solution in pyridine, direct evidence of combination of iodine with the solvent has been obtained by the isolation of a crystalline compound (Waentig, *loc. cit.*). In others, the brown colour is probably due in a large measure to iodine compounds which are formed as a result of double decomposition. Acetone, which has been frequently used as a solvent for iodine in investigations relating to the cause of the differences in colour exhibited by iodine solutions, belongs to this class.

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* These changes in volume refer to the liquid solute.

It has been shown (Dawson and Leslie, Trans., 1909, **95**, 1860) that iodine reacts rapidly with acetone, forming hydrogen iodide and acetone, and that a condition of equilibrium is established as a consequence of the reversibility of the reaction. In the case of a solution, prepared by dissolving one gram-molecule of iodine in 100 gram-molecules of acetone, about 45 per cent. of the iodine is converted into hydrogen iodide. In the resulting solution, the iodine, which has not been acted on by the acetone, is largely combined with the hydrogen iodide in the form of a polyiodide, and, in all probability, the colour and the absorption spectrum of this solution correspond with that of iodine, which is thus combined with one of the products resulting from the interaction of the solute and the solvent. Other ketones react similarly with iodine, and it is not unlikely that the colour of solutions of iodine in other solvents may be in part due to the same cause.

These facts add weight to the conclusion that solutions of iodine do not, in general, belong to the type of "normal" solutions as defined in this paper, and on this account the absence of any general connexion between the measured changes in volume and the formation of these solutions and the internal pressures and compressibilities of the solvents is not surprising. It may be that solutions of naphthalene approximate more closely to this type, but, in any case, the observed lack of parallelism between the volume changes for these two substances in the same series of solvents is consistent with the view that the dissolved substances combine to an appreciable extent with the various solvents.

PHYSICAL CHEMISTRY LABORATORY,
THE UNIVERSITY,
LEEDS.

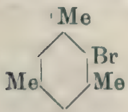
CCII.—*The Constitution of the Benzenetetracarboxylic Acids.*

By HANNAH BAMFORD and JOHN LIONEL SIMONSEN.

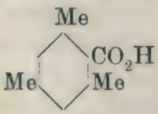
DURING the course of an investigation which is described in the succeeding paper (p. 1910), it became necessary definitely to determine the constitution of two of the benzenetetracarboxylic acids, namely, prehnitic and mellophanic acids. The three isomeric benzenetetracarboxylic acids were first obtained by Baeyer (*Annalen*, 1873, **166**, 325) during the course of his classical researches on mellitic acid. It is unnecessary here to enter into the reasoning by which he deduced the formulæ to be ascribed to these acids, and it will suffice to point out that whilst he proved conclusively (*loc. cit.*, p. 344) pyromellitic acid to be benzene-1 : 2 : 4 : 5-tetracarboxylic acid, he was unable to decide whether prehnitic acid was benzene-1 : 2 : 3 : 4- or -1 : 2 : 3 : 5-tetracarboxylic acid. He inclined to the latter view, however (*loc. cit.*, p. 344), because he found that this acid only yields a monoanhydride, whilst if it had possessed four adjacent carboxyl groups it should give a dianhydride.

The question remained undecided until O. Jacobsen (*Ber.*, 1884, **17**, 2517) by the oxidation of *iso*durene obtained an acid which was shown by direct comparison to be identical with Baeyer's mellophanic acid. Now, since *iso*durene was obtained from bromomesitylene, it followed that mellophanic acid must be benzene-1 : 2 : 3 : 5-tetracarboxylic acid, and hence prehnitic acid would be the 1 : 2 : 3 : 4-isomeride. Further evidence in support of this view was obtained by Töhl (*Ber.*, 1888, **21**, 907), who oxidised prehnitene and isolated an acid which showed all the properties of prehnitic acid.

As the present authors had obtained results which seemed to throw some doubt on these experiments, it was decided to endeavour to devise methods for preparing prehnitic and mellophanic acids which would leave no doubt as to their constitution.



(I.)



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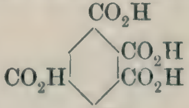

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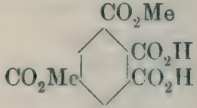

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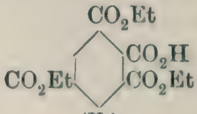

(V.)

A ready means of carrying this out appeared to be to prepare mesitylenecarboxylic acid and to oxidise this to the corresponding tetrabasic acid.

Mesitylenecarboxylic acid (II) was found to be most conveniently obtained by the action of magnesium and carbon dioxide on bromomesitylene (I), and on oxidation with nitric acid under the conditions described in the experimental part of this paper (p. 1907), it was found to be converted quantitatively into benzene-1 : 2 : 3 : 5-tetracarboxylic acid (III).

The substance obtained in this way showed all the properties ascribed by Baeyer to the acid called by him prehnitic acid, and there can therefore be little doubt that this acid is really benzene-1 : 2 : 3 : 5-tetracarboxylic acid. This view also receives support from the following stereochemical considerations : (*a*) The acid yields only a monoanhydride (Baeyer, *loc. cit.*); (*b*) when esterified in the cold with methyl alcohol and hydrochloric acid it gives a dimethyl ester (compare Meyer and Sudborough, *Ber.*, 1894, **27**, 1591), which probably has the constitution (IV); (*c*) when, however, the acid is esterified by means of alcohol and sulphuric acid by heating on the water-bath in the usual manner, it yields a triethyl ester which undoubtedly has the constitution (V).

Having shown conclusively that prehnitic acid is benzene-1 : 2 : 3 : 5-tetracarboxylic acid, it seemed that mellophanic acid must be benzene-1 : 2 : 3 : 4-tetracarboxylic acid, but in order to be certain it was decided to synthesise this acid.

For this purpose a large amount of 1 : 4-dimethylnaphthalene was prepared, and this, on oxidation with nitric acid, gave a mixture of acids, from which a tetrabasic acid was separated; this possessed all the properties of Baeyer's mellophanic acid.

When the silver salt of the acid was heated with methyl iodide, a neutral tetramethyl mellophanate (m. p. 133°) was obtained.

Since mellophanic acid is 1 : 2 : 3 : 4-benzenetetracarboxylic acid, it should, in accordance with the usual views on steric hindrance, yield only a diacid ester by the direct process of esterification. This is probably the case, since no trace of neutral tetraethyl mellophanate was produced on heating the acid with alcohol and sulphuric acid. A barium salt was isolated by treatment of the reaction product with baryta and subsequent evaporation, and this gave on titration results which indicated it to be a barium salt of the diacid ester with two or three molecules of water of crystallisation. The direct determination of the water of crystallisation gave entirely anomalous results, and this important point will therefore be reinvestigated. It is clear, however, that the acid cannot be completely esterified by the usual process.

As the result of these experiments there can therefore be little doubt that prehnitic acid and mellophanic acid are respectively benzene-1 : 2 : 3 : 5- and -1 : 2 : 3 : 4-tetracarboxylic acids.

It is somewhat difficult to see how Jacobsen (*loc. cit.*) obtained from *iso*durene the acid which he showed to be identical with Baeyer's mellophanic acid, since he prepared his hydrocarbon by the action of methyl iodide and sodium on bromomesitylene. It is hardly likely that any rearrangement of groups would take place during this reaction, as such rearrangement only appears to take place in the presence of aluminium chloride. We are therefore driven to the conclusion that the hydrocarbon used by Jacobsen in his experiments cannot have been mesitylene, and must have consisted mainly of ψ-cumene.

It has already been mentioned that Töhl (*loc. cit.*) obtained prehnitic acid by the oxidation of prehnitene, which hydrocarbon is prepared by the degradation of pentamethylbenzene by means of sulphuric acid. He, however, offers no proof of the constitution of his hydrocarbon apart from the fact that it was identical with that previously obtained by Jacobsen (*Ber.*, 1886, **19**, 1213; 1887, **20**, 901). Jacobsen isolated this hydrocarbon by the action of hydrochloric acid on a sulphonamide prepared from durene and by the degradation of pentamethylbenzene, two reactions which offer no proof of constitution, and the only grounds for considering that prehnitene is 1 : 2 : 3 : 4-tetramethylbenzene is because it is isomeric with the hydrocarbon he obtained by the action of methyl iodide and sodium on bromomesitylene, and that it does not give pyromellitic acid on oxidation. If, then, the hydrocarbon obtained by Jacobsen from bromomesitylene is 1 : 2 : 3 : 4-tetramethylbenzene, then prehnitene must be 1 : 2 : 3 : 5-tetramethylbenzene.

Further experiments on this interesting subject are in progress. Unfortunately, the wrong conception of the nature of prehnitic acid and of prehnitene, which has so long prevailed, has led to much confusion in assigning constitutional formulæ on the basis of these substances being 1 : 2 : 3 : 4-substitution derivatives of benzene.

EXPERIMENTAL.

Prehnitic Acid (*Benzene*-1 : 2 : 3 : 5-*tetracarboxylic Acid*).

Mesitylenecarboxylic Acid.—Bromomesitylene (20 grams) was added to magnesium (2·4 grams) suspended in dry ether, the magnesium having first been treated with a small amount of methyl iodide in order to render it reactive. A vigorous reaction ensued, and when this had ceased, the mixture was heated on the water-bath until all the magnesium had passed into solution. After being kept cold overnight, a slow stream of dry carbon dioxide was passed into the ethereal solution of the magnesium compound, when a heavy oil slowly separated. Ice and dilute hydrochloric acid were then added, and the ethereal layer was separated and washed with sodium carbonate solution.

On acidifying the latter solution, a colourless, crystalline precipitate (7·5 grams) separated, which was collected and dried. The mesitylenecarboxylic acid obtained in this way was purified by crystallisation from light petroleum, from which it separated in glistening prisms, possessing the correct melting point, 151—152°. (Found, $C=72·9$; $H=7·4$. Calc., $C=73·4$; $H=7·3$ per cent.)

Oxidation of Mesitylenecarboxylic Acid to Prehnitic Acid.—Mesitylenecarboxylic acid (1 gram) was mixed with 10 c.c. of dilute nitric acid (D 1·15), and heated in a sealed tube for eight hours at 170—180°. After removing the nitric acid by evaporation on the water-bath, the prehnitic acid was purified by repeated crystallisation from hydrochloric acid, from which it separated in small prisms. After drying at 100° to remove water of crystallisation, it was analysed. (Found, $C=46·8$; $H=2·3$. Calc., $C=47·2$; $H=2·3$ per cent.)

Prehnitic acid melts at 252°, previously softening at about 240°, and is converted into the anhydride, melting at 238°, whereas Baeyer (*Annalen*, 1873, **166**, 328) states that it begins to melt at 237°, becoming completely liquid at 250°, whilst the anhydride melts at 238°. That it was a tetrabasic acid was shown by titration with standard sodium hydroxide, when it was found that 0·096 neutralised 0·058NaOH, whereas a tetrabasic acid, $C_{10}H_6O_8$, should neutralise 0·06008NaOH. When barium chloride was added to an aqueous solution of prehnitic acid and the solution warmed, an immediate precipitate of the barium salt of the acid was obtained. After drying at the temperature of the laboratory for two days, it was analysed, when it was found to have the composition given to the barium salt of prehnitic acid by Baeyer (*Annalen*, 1873, **166**, 332):

0·2354 lost 0·0122 H_2O at 100°. $H_2O=5·2$.
0·1514 gave 0·0502 $BaSO_4$. $Ba=19·4$.
$(C_{10}H_5O_8)_2Ba,3H_2O$ requires $Ba=19·6$; $2H_2O=5·4$ per cent.

The barium salt, when dried at 100°, gave the following result:

0·2197 gave 0·0775 $BaSO_4$. $Ba=20·70$.
$(C_{10}H_5O_8)_2Ba,H_2O$ requires $Ba=20·8$ per cent.

Tetramethyl Prehnitate, $C_6H_2(CO_2Me)_4$.—Tetramethyl prehnitate has already been isolated by Baeyer (*Annalen*, 1873, **166**, 333) by the action of methyl iodide on the silver salt of the acid. A repetition of this process yielded the ester in beautiful, colourless needles, which, after crystallisation from methyl alcohol, melted at 108—109° (Baeyer gives 104—109°). (Found, $C=54{\cdot}1$; $H=4{\cdot}5$. Calc., $C=54{\cdot}2$; $H=4{\cdot}5$ per cent.)

Triethyl Hydrogen Prehnitate, $C_6H_2(CO_2Et)_3{\cdot}CO_2H$.

This ester, which does not seem to have been previously obtained, is readily formed when prehnitic acid is treated with alcohol and sulphuric acid in the usual manner. It was purified by repeated crystallisation from a mixture of benzene and light petroleum, when it separated in colourless clusters of needles, which melt at about 108—110°:

0·123 gave 0·2625 CO_2 and 0·0601 H_2O. $C=58{\cdot}2$; $H=5{\cdot}4$.

$C_{17}H_{18}O_8$ requires $C=58{\cdot}3$; $H=5{\cdot}1$ per cent.

Triethyl hydrogen prehnitate is readily soluble in most organic solvents with the exception of light petroleum. Its probable constitution has already been discussed in the introduction (p. 1905).

Dimethyl Dihydrogen Prehnitate, $C_6H_2(CO_2Me)_2(CO_2H)_2$.*

It has already been pointed out by Meyer and Sudborough (*Ber.*, 1894, **27**, 159) that when a methyl-alcoholic solution of prehnitic acid is treated with hydrogen chloride in the cold, only a dimethyl ester is formed. This result has been confirmed, but the melting point of the ester when crystallised from a mixture of acetone and light petroleum was found to be about 191°, and not 176—177°, as stated by them. The *silver* salt was analysed:

0·0519 gave 0·0225 Ag. $Ag=43{\cdot}3$.

$C_{12}H_8O_8Ag_2$ requires $Ag=43{\cdot}5$ per cent.

Mellophanic Acid (*Benzene*-1 : 2 : 3 : 4-*tetracarboxylic Acid*).

Oxidation of 1 : 4-*Dimethylnaphthalene.*—1 : 4-Dimethylnaphthalene (2 c.c.), prepared as described by Giovannozzi (*Gazzetta*, 1882, **12**, 147), was mixed with 40 per cent. nitric acid (20 c.c.), and heated in a sealed tube at 170—180° for eight hours. The clear solution was evaporated to dryness on the water-bath, when a semi-solid, crystalline mass was obtained, which evidently consisted of a mixture of acids.

In order to separate the mellophanic acid, a somewhat tedious process of purification had to be adopted. The crude acid was dissolved in as little water as possible, and the solution treated with excess of stannous chloride and concentrated hydrochloric acid for two hours on the water-bath. The strongly acid mixture was then evaporated to dryness, the residue dissolved in water, and the tin precipitated with hydrogen sulphide. After separating the tin sulphide, the solution was again evaporated to dryness, and the mixture of phthalic and mellophanic acids extracted with dry ether in a Soxhlet apparatus, when it was found that the amino-acids, which were present as hydrochlorides, were not dissolved. As preliminary experiments showed it to be a matter of some difficulty to separate the mellophanic and phthalic acids by fractional crystallisation, they were converted into their silver salts in the usual manner, and the dry silver salts were digested with methyl iodide in benzene solution for some hours on the water-bath. After separating from the silver iodide, the benzene was removed, when a viscid oil was obtained, which on trituration with ether partly solidified. The solid ester, which was found to consist of *methyl mellophanate*, was separated and purified by repeated crystallisation from methyl alcohol:

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* By an oversight, Stewart states (*Stereochemistry*, p. 341) that prehnitic acid forms a tetramethyl ester when esterified in the usual manner.

0·124 gave 0·2455 CO_2 and 0·0552 H_2O. $C=54·0$; $H=4·9$.

$C_{14}H_{14}O_8$ requires $C=54·2$; $H=4·5$ per cent.

Methyl mellophanate, which does not appear to have been previously described, separates from methyl alcohol in long, glistening needles, melting at 133—135°. It is readily soluble in benzene, ethyl acetate, or acetone, but only sparingly so in ether, light petroleum, or cold methyl alcohol.

In order to obtain the free acid, the methyl ester was hydrolysed in the usual manner with alcoholic potassium hydroxide, and, after removing the alcohol on the water-bath, the solution was acidified, evaporated to dryness, and the acid extracted with ether in a Soxhlet apparatus. The crude acid was purified by crystallisation from hydrochloric acid, when it was found to soften slightly at 225°, and melt and decompose at 238° with formation of the anhydride (compare Baeyer, *loc. cit.*). (Found, $C=47·02$; $H=2·3$. Calc., $C=47·2$; $H=2·3$ per cent.) The basicity of the acid was determined by titration with normal sodium hydroxide, when it was found that 0·0648 neutralised 0·0404NaOH, whereas a tetrabasic acid, $C_{10}H_6O_8$, should neutralise 0·04081NaOH.

Mellophanic acid is readily soluble in water or acetone, but only sparingly so in most organic solvents.

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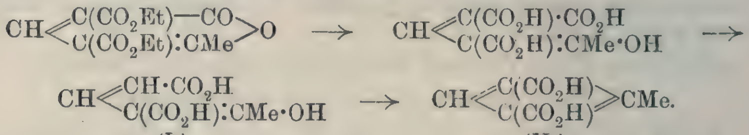
CCIII.—*Ethyl 6-Methyl-2-pyrone-3 : 5-dicarboxylate and its Conversion into Methyltrimesic Acid.*

By JOHN LIONEL SIMONSEN.

IN a recent communication (Trans., 1908, **93**, 1022) the author described the preparation of ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate, and pointed out that on hydrolysis with alkaline reagents it gave rise to an acid to which the empirical formula $C_7H_6O_4$ was given, and it was suggested that this might possibly be 1-methyl-$\Delta^{1:3}$-*cyclo*butadiene-2 : 4-dicarboxylic acid, internal condensation having taken place in the following manner:



$$\mathrm{CH}{<}\begin{matrix}\mathrm{C(CO_2Et)—CO}\\ \mathrm{C(CO_2Et){:}CMe}\end{matrix}{>}\mathrm{O} \longrightarrow \mathrm{CH}{<}\begin{matrix}\mathrm{C(CO_2H)\cdot CO_2H}\\ \mathrm{C(CO_2H){:}CMe\cdot OH}\end{matrix} \longrightarrow$$

$$\underset{\text{(I.)}}{\mathrm{CH}{<}\begin{matrix}\mathrm{CH\cdot CO_2H}\\ \mathrm{C(CO_2H){:}CMe\cdot OH}\end{matrix}} \longrightarrow \underset{\text{(II.)}}{\mathrm{CH}{<}\begin{matrix}\mathrm{C(CO_2H)}\\ \mathrm{C(CO_2H)}\end{matrix}{>}\mathrm{CMe.}}$$

Since an acid possessing this constitution would be of theoretical interest from several points of view, further experiments were instituted with the object of subjecting it to a more searching investigation.

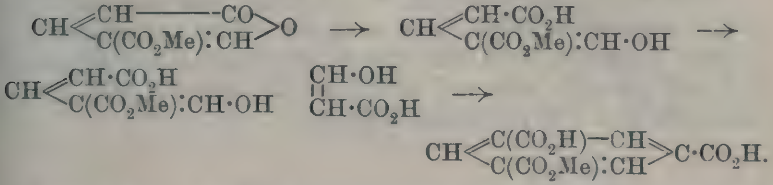
It seemed, in the first place, desirable to devise a means of directly synthesising the ethyl ester of α-acetylglutaconic acid (I), since, if the above reasoning were correct, this ester should, on treatment with suitable reagents, readily be converted into 1-methyl-$\Delta^{1:3}$-*cyclo*butadiene-2 : 4-dicarboxylic acid (II). This synthesis was easily carried out by the condensation of ethyl propiolate and ethyl sodioacetoacetate, when the reaction proceeds quite normally with the formation of ethyl α-acetylglutaconate,

$$\mathrm{CO_2Et\cdot C{⋮}CH + CH_2Ac\cdot CO_2Et} \longrightarrow \underset{\text{(I.)}}{\mathrm{CO_2Et\cdot CH{:}CH\cdot CHAc\cdot CO_2Et}},$$

the reaction proceeding on somewhat similar lines to the condensation of ethyl phenylpropiolate and ethyl acetoacetate so exhaustively investigated by Ruhemann (Trans., 1899, **75**, 251).

At the same time, however, a further reaction takes place, and a small quantity of a crystalline solid was isolated, which melted at 48°, and was found to be identical with the ethyl ester of the acid previously obtained by the hydrolysis of ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate (*loc. cit.*, p. 1028). The isolation of this ester was at first thought to be additional evidence in favour of the original view of the constitution of the acid $C_7H_6O_4$, which was, moreover, supported by the fact that ethyl α-acetylglutaconate, on hydrolysis with barium hydroxide, yielded, besides glutaconic acid, a small quantity of the same acid (see p. 1914). As the result of further experiments this view had to be abandoned, and the conclusion was drawn that this acid, supposed to be $C_7H_6O_4$, was in all probability a methylbenzenetricarboxylic acid, $C_{10}H_8O_6$.

During the course of his classical investigation of coumalinic acid, von Pechmann (*Annalen*, 1891, **264**, 293) showed that when the methyl ester of coumalinic acid was hydrolysed with aqueous sodium hydroxide it was converted into the monomethyl ester of trimesic acid, the reaction taking place on the following lines:

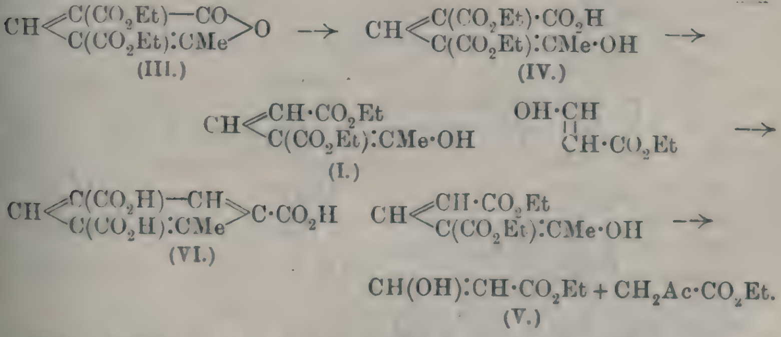


$$\mathrm{CH}{<}\begin{matrix}\mathrm{CH{-\!-\!-}CO}\\ \mathrm{C(CO_2Me){:}CH}\end{matrix}{>}\mathrm{O} \longrightarrow \mathrm{CH}{<}\begin{matrix}\mathrm{CH{\cdot}CO_2H}\\ \mathrm{C(CO_2Me){:}CH{\cdot}OH}\end{matrix} \longrightarrow$$

$$\mathrm{CH}{<}\begin{matrix}\mathrm{CH{\cdot}CO_2H}\\ \mathrm{C(CO_2Me){:}CH{\cdot}OH}\end{matrix} \quad \begin{matrix}\mathrm{CH{\cdot}OH}\\ \|\\ \mathrm{CH{\cdot}CO_2H}\end{matrix} \longrightarrow$$

$$\mathrm{CH}{<}\begin{matrix}\mathrm{C(CO_2H){-}CH}\\ \mathrm{C(CO_2Me){:}CH}\end{matrix}{>}\mathrm{C{\cdot}CO_2H}.$$

Taking these facts into consideration, it appeared probable that the hydrolysis of ethyl 6-methyl-2-pyrone-3:5-dicarboxylate had proceeded in an analogous manner with the formation of a methyltrimesic acid:



$$\underset{\text{(III.)}}{\mathrm{CH}{<}\begin{matrix}\mathrm{C(CO_2Et){-}CO}\\ \mathrm{C(CO_2Et){:}CMe}\end{matrix}{>}\mathrm{O}} \longrightarrow \underset{\text{(IV.)}}{\mathrm{CH}{<}\begin{matrix}\mathrm{C(CO_2Et){\cdot}CO_2H}\\ \mathrm{C(CO_2Et){:}CMe{\cdot}OH}\end{matrix}} \longrightarrow$$

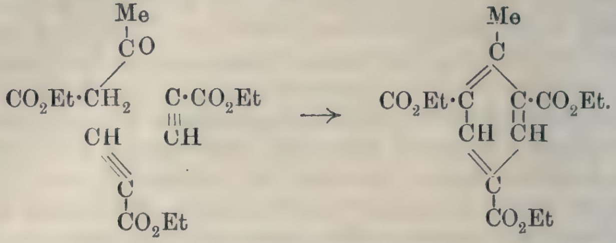
$$\underset{\text{(I.)}}{\mathrm{CH}{<}\begin{matrix}\mathrm{CH{\cdot}CO_2Et}\\ \mathrm{C(CO_2Et){:}CMe{\cdot}OH}\end{matrix}} \quad \begin{matrix}\mathrm{OH{\cdot}CH}\\ \|\\ \mathrm{CH{\cdot}CO_2Et}\end{matrix} \longrightarrow$$

$$\underset{\text{(VI.)}}{\mathrm{CH}{<}\begin{matrix}\mathrm{C(CO_2H){-}CH}\\ \mathrm{C(CO_2H){:}CMe}\end{matrix}{>}\mathrm{C{\cdot}CO_2H}} \quad \mathrm{CH}{<}\begin{matrix}\mathrm{CH{\cdot}CO_2Et}\\ \mathrm{C(CO_2Et){:}CMe{\cdot}OH}\end{matrix} \longrightarrow$$

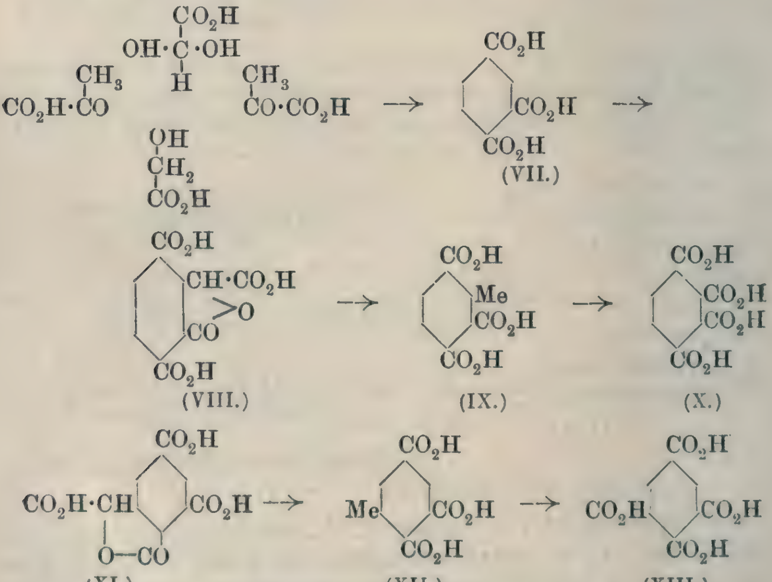
$$\underset{\text{(V.)}}{\mathrm{CH(OH){:}CH{\cdot}CO_2Et}} + \mathrm{CH_2Ac{\cdot}CO_2Et}.$$

The 2-pyrone (III) is converted, in the first place, into the diethyl ester of α′-carboxy-α-acetylglutaconic acid (IV), which, with loss of carbon dioxide, passes into ethyl α-acetylglutaconate (I). Half of the ethyl α-acetylglutaconate then undergoes decomposition into ethyl formylacetate (V) and ethyl acetoacetate, and the ethyl formylacetate thus generated combines with the unchanged ethyl α-acetylglutaconate, with loss of two molecules of water and formation of *methyltrimesic acid* (VI).

If this constitution be accepted for the acid, the formation of its ethyl ester by the interaction of ethyl propiolate and ethyl acetoacetate is readily explained. It may be assumed that two molecules of ethyl propiolate condense with one of ethyl acetoacetate in accordance with the following scheme:



On examining the literature, it was found that only one other methylbenzenetricarboxylic acid is known. This was obtained by Doebner (*Annalen*, 1900, **311**, 136) by the condensation of pyruvic acid and glyoxylic acid and fusion of the resulting phthalidetricarboxylic acid with potassium hydroxide:



(VII.) (VIII.) (IX.) (X.) (XI.) (XII.) (XIII.)

Doebner considered that benzene-1 : 2 : 4-tricarboxylic acid (VII) was first formed, which then condensed with a further molecule of glyoxylic acid to give phthalidetricarboxylic acid (VIII), and this, on subsequent fusion with potassium hydroxide, gave 1-methylbenzene-2 : 3 : 6-tricarboxylic acid (IX). He based this view of the constitution on the fact that on oxidation with potassium permanganate, phthalidetricarboxylic acid gave prehnitic acid, which be regarded as benzene-1:2:3:4-tetracarboxylic acid (X). Now, since it has been shown in the preceding communication (p. 1904) that prehnitic acid is benzene-1:2:3:5-tetracarboxylic acid (XIII), it follows that the acid obtained by Doebner cannot be 1-methylbenzene-2:3:6-tricarboxylic acid.

Probably the condensation described by Doebner proceeds on the following lines. Benzene-1:2:4-tricarboxylic acid (VII) is first formed, and this then condenses with glyoxylic acid to give the isomeric phthalidetricarboxylic acid (XI), which, on fusion with potassium hydroxide, would give 1-methylbenzene-2:3:5-tricarboxylic acid (XII), and on oxidation with potassium permanganate, prehnitic acid (XIII). This view of the condensation is also more probable on stereochemical grounds.

In order to leave no doubt as to the constitution of the methyltrimesic acid obtained in this investigation, it was oxidised with nitric acid or potassium permanganate, when the tetracarboxylic acid was formed, and was shown to be in every way identical with prehnitic acid (benzene-1:2:3:5-tetracarboxylic acid).

EXPERIMENTAL.

Condensation of Ethyl Acetoacetate and Ethyl Propiolate.

Formation of Ethyl Methyltrimesate and Ethyl α-Acetylglutaconate.

Sodium (1·3 grams) was dissolved in alcohol, and, after the addition of ethyl acetoacetate (7·8 grams), ethyl propiolate (5·9 grams) was added to the well-cooled solution. Much heat was generated, and the reaction mixture rapidly became deep red. After being kept overnight, water was added, and the oil which separated was dissolved in ether, and the ethereal solution washed, dried, and evaporated. The residual oil was carefully fractionated under diminished pressure (14 mm.), when, after a small amount of unchanged ethyl acetoacetate had passed over, it was found to distil between 210° and 220°. The distillate (3 grams) was cooled in a freezing mixture, when it rapidly solidified, and after draining on porous porcelain it was crystallised from light petroleum, when it melted at 48°:

0·1315 gave 0·3013 CO_2 and 0·0796 H_2O. C=62·5; H=6·7.

$C_{16}H_{18}O_6$ requires C=62·7; H=5·9 per cent.

The *ethyl methyltrimesate* obtained in this manner was found to be in every respect identical with that previously described (*loc. cit.*, p. 1028), and a mixture of the two melted sharply at 48°.

In order to remove any doubt as to the identity of these two substances, a small quantity of the pure ester (1 gram) was hydrolysed with dilute hydrochloric acid, and after removing the excess of hydrochloric acid by evaporation, the *methyltrimesic acid* was purified by repeated crystallisation from hot water. After drying at 110°, it was analysed:

0·1097 gave 0·2152 CO_2 and 0·0395 H_2O. C=53·5; H=4·0.

$C_{10}H_8O_6$ requires C=53·6; H=3·6 per cent.

On melting, it behaved in the manner characteristic of this acid, commencing to sinter at 268°, and decomposing completely at 300°.

The alkaline mother liquor, from which the ethyl methyltrimesate had been separated, was rendered just acid with dilute hydrochloric acid, when an oil separated. This was dissolved in ether, the ethereal solution washed with dilute sodium carbonate,* dried, and evaporated, and the residual yellow oil fractionated under diminished pressure (12 mm.), when it was found to distil very constantly at 158—160°. Yield 5 grams:

0·1535 gave 0·3244 CO_2 and 0·0997 H_2O. C=57·6; H=7·2.

$C_{11}H_{16}O_5$ requires C=57·9; H=7·0 per cent.

Ethyl α-acetylglutaconate, which does not appear to have been previously described, is a colourless oil, possessing a pleasant ethereal odour. Its alcoholic solution gives with ferric chloride an intense purple-violet coloration.

Hydrolysis of Ethyl α-Acetylglutaconate.—For the hydrolysis of this ester, barium hydroxide was found to yield the most satisfactory results.

Ethyl acetylglutaconate (5 grams) was mixed with a concentrated solution of barium hydroxide [10 grams crystallised $Ba(OH)_2$], and after boiling for two hours on the sand-bath, the canary-yellow solution was cooled and extracted ten times with pure ether. On removing the ether an oil was obtained which rapidly solidified, and after draining on porous porcelain was crystallised from dry ether, when it was found to separate in two distinct forms, consisting of fine, colourless needles and small, hard, yellow nodules. These were separated, as far as possible, mechanically, and the needles, which weighed less than 0·1 gram, were found to consist of methyltrimesic acid, since they showed the characteristic melting point of this acid, and when esterified with methyl alcohol and sulphuric acid yielded an ester melting at 107°.

The main portion of the acid, which separated in hard, yellow nodules, was purified by repeated crystallisation from ether with the aid of animal charcoal, when it was obtained in colourless prisms, melting at 138°, and evidently consisted of glutaconic acid, which melts at this temperature (Buchner, *Ber.*, 1890, **23**, 703). (Found, C=45·9; H=4·7. Calc., C=46·2; H=4·6 per cent.)

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* The sodium carbonate washings, on acidification, yielded a small amount of a viscid oil which was not further investigated.

Methyltrimesic Acid, $CH_3\cdot C_6H_2(CO_2H)_3$.

The properties of methyltrimesic acid have already been described (*loc. cit.*, p. 1027), but in view of the somewhat unsatisfactory analytical data obtained, further experiments were instituted with the view of obtaining this acid in a purer state. As it was not readily purified by repeated crystallisation from hot water, the acid was dissolved in a slight excess of sodium carbonate and oxidised with a dilute solution of potassium permanganate in the cold until a permanent pink colour was obtained. After removing the excess of potassium permanganate with sulphur dioxide, the manganese dioxide was removed, and the alkaline solution concentrated and acidified. The precipitated acid was collected and repeatedly crystallised from hot water, from which it separates, when pure, in long, prismatic needles, melting at the temperature previously given:

0·1606 gave 0·3146 CO_2 and 0·0532 H_2O. C=53·5; H=3·7.
0·1392 „ 0·2747 CO_2 and 0·0459 H_2O. C=53·8; H=3·6.
$C_{10}H_8O_6$ requires C=53·6; H=3·6 per cent.

The *silver* salt separates as a caseous, white precipitate when silver nitrate is added to a faintly alkaline solution of the ammonium salt. After drying at 100°, it was analysed:

0·1915 gave 0·114 Ag. Ag=59·5.
$C_{10}H_5O_6Ag_3$ requires Ag=59·4 per cent.

Methyl Methyltrimesate.—This ester, which has been previously described, when pure melts at 107°, and not at 106° (*loc. cit.*, p. 1028). A pure specimen was prepared for the determination of the refractive index; on analysis it gave the following figures:

0·1349 gave 0·2888 CO_2 and 0·0626 H_2O. C=58·4; H=5·1.
$C_{13}H_{14}O_6$ requires C=58·6; H=5·2 per cent.

Methyl methyltrimesate is also obtained in a yield of 96·5 per cent. when methyltrimesic acid is esterified by the method used by Meyer and Sudborough (*Ber.*, 1894, **27**, 1591). The acid (0·5 gram) was dissolved in methyl alcohol (10 c.c.), and the solution saturated in the cold with hydrogen chloride. The acid immediately separated out, but on keeping in the cold slowly redissolved, and after twelve hours the liquid was filled with a mass of felted needles. These were dissolved in ether, when 0·56 gram of the methyl ester was obtained. This result is of some interest, as, from stereochemical considerations, it seemed unlikely that the trimethyl ester would be formed, especially since under similar conditions prehnitic acid only yields a dimethyl ester (see p. 1908).

Mr. R. T. Hardman kindly carried out a molecular-weight determination of this ester by the cryoscopic method, benzene being used as the solvent:

0·267, in 17·537 benzene, gave $\Delta t = -0·3°$. M.W. = 253·7.
0·4052 ,, 17·57 ,, ,, $\Delta t = -0·456°$. M.W. = 253·0.
$C_{13}H_{14}O_6$ requires M.W. = 266.

I am much indebted to Dr. Ida Smedley for very kindly determining the refractive power of this ester. The determination was carried out in chloroform solution:

Percentage strength of solution.	M_{α}.	M_{β}.	M_{γ}.	$M_{\gamma-\alpha}$.
6·5986	65·47	67·77	68·79	3 32

Calculated value $C_{13}H_{14}O''_3O'_3$ 311 = 63·23.

It seems likely that the high value is due to the conjugation of the carbonyl groups with the benzene ring.

Distillation of the Barium Salt of Methyltrimesic Acid.—The barium salt (30 grams) was mixed with barium oxide (120 grams), and carefully distilled from a retort, when an oil slowly passed over. This was purified by repeated distillation over sodium, when it was found to boil constantly at 110°, and evidently consisted of nearly pure toluene. (Found, C = 90·7; H = 8·7. Calc., C = 91·3; H = 8·7 per cent.)

Oxidation of Methyltrimesic Acid to Prehnitic Acid.

I. *With Nitric Acid.*—Methyltrimesic acid (2 grams) was mixed with 40 per cent. nitric acid (20 c.c.), and heated in a sealed tube for six hours at 170—180°. The clear solution was evaporated to dryness, and the solid acid thus obtained was purified by repeated crystallisation from hydrochloric acid, when it separated in microscopic prisms. After drying at 100°, it was analysed. (Found, C = 47·2; H = 2·5. Calc., C = 47·2; H = 2·3 per cent.) Prehnitic acid obtained in this manner melted at 250—251°, softening slightly at 247°, with formation of the anhydride, which melted at 238°. It was found to be identical in every way with prehnitic acid, obtained by the oxidation of mesitylenecarboxylic acid (see p. 1907). The basicity of the acid was determined by titration with standard sodium hydroxide, when 0·1095 of the acid neutralised 0·068NaOH, whereas this amount of a tetrabasic acid, $C_{10}H_6O_8$, should neutralise 0·0685NaOH.

II. *With Potassium Permanganate.*—In carrying out this oxidation, methyltrimesic acid (5 grams) was dissolved in a slight excess of dilute sodium carbonate solution, and after the addition of potassium permanganate (10 grams) dissolved in water (500 c.c.), the mixture was boiled in a reflux apparatus for twelve hours, when the oxidation was complete. After removing the manganese dioxide, the alkaline solution was concentrated on the water-bath, acidified, and extracted several times with ether, the ethereal solution being dried and evaporated. The crystalline acid thus obtained was purified by crystallisation from hydrochloric acid, when it was found to melt at 250—251°, with formation of the anhydride, which melted at 238°. This acid was in every way identical with that obtained in the oxidation with nitric acid. The silver salt separates as a caseous, white precipitate on the addition of silver nitrate to a slightly alkaline solution of the ammonium salt. (Found, $C=17{\cdot}2$; $H=0{\cdot}7$; $Ag=62{\cdot}9$. Calc., $C=17{\cdot}6$; $H=0{\cdot}3$; $Ag=63{\cdot}4$ per cent.)

In order to leave no doubt as to the identity of this acid with prehnitic acid, the characteristic barium salt was prepared by the addition of barium chloride to a warm aqueous solution of the acid. After drying for two days in the air it was analysed. (Found, $Ba=19{\cdot}6$; $H_2O=5{\cdot}0$. $(C_{10}H_5O_8)_2Ba,3H_2O$ requires $Ba=19{\cdot}6$; $2H_2O=5{\cdot}4$ per cent.) It was also analysed after being dried at 100°. (Found, $Ba=20{\cdot}6$. $(C_{10}H_5O_8)_2Ba,H_2O$ requires $Ba=20{\cdot}8$ per cent.)

Tetramethyl prehnitate was prepared in the usual manner by the action of methyl iodide on the silver salt of the acid, and after crystallisation from methyl alcohol melted at 108—109°. (Found, $C=53{\cdot}7$; $H=4{\cdot}6$. Calc., $C=54{\cdot}2$; $H=4{\cdot}5$ per cent.)

The author wishes to thank the Research Fund Committee of the Chemical Society for a grant which has defrayed much of the expense of this and the preceding communication.

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CCIV.—*The Volatile Constituents of Coal.*

By MAURICE JOHN BURGESS and RICHARD VERNON WHEELER.

THIS investigation into the nature of the "volatile constituents" of coal has been undertaken in connexion with experiments now being conducted by the Mining Association of Great Britain. These experiments—"the British Coal Dust Experiments"—have for their object the study of the phenomena occurring during the explosive combustion of mixtures of fine coal dust and air, with a view to discover a means of preventing such explosions.

An investigation into the nature of the volatile constituents of coal is of particular value in connexion with such a problem, because of the obvious relationship that exists between the behaviour on heating of the volatile matter contained in any sample of coal and the degree of inflammability of the coal dust.

By determining such factors as (*a*) the temperature at which gas is most readily evolved, (*b*) the stage in the heating at which the most inflammable mixture of gases makes its appearance, and (*c*) the shortest time of heating that will allow any gas at all to be distilled, it should be possible to draw a distinction between dusts of different degrees of inflammability or liability to propagate explosion.

The interest that attaches to the study of the action of heat on coal, however, is not confined to any particular problem, and, although in carrying out the present investigation we have had the problem of coal dust explosions alone in mind, we believe that the experimental methods adopted render our results of more widespread application.

We hope ultimately to obtain definite information regarding the composition and chemical constitution of coal.

Destructive Distillation of Coal at Different Temperatures.

This part of our investigations, the ultimate object of which is the elucidation of the nature of "coal," yields only a little information in that direction when considered by itself. We find it necessary, therefore, to reserve our conclusions regarding the composition of coal for a future communication, and merely to indicate the bearing that this part of our work has on the subject.

The principal facts brought to light by the distillation of different samples of coal at different temperatures are as follows:

1. With all coals, whether bituminous, semi-bituminous, or anthracite, there is a well-defined decomposition point, at a temperature lying between 700° and 800°, which corresponds with a marked increase in the quantity of hydrogen evolved. With bituminous coals, the increase in the quantity of hydrogen evolved falls off at temperatures above 900°, but with anthracitic coals it is maintained up to 1100°.

2. Evolution of hydrocarbons of the paraffin series ceases practically entirely at temperatures above 700°.

3. Ethane, propane, and butane, and, probably, higher members of the paraffin series form a large percentage of the gases evolved at temperatures below 450°.

From these facts it may be concluded that coal of whatever geological age contains a compound which undergoes decomposition at temperatures above 700° (under atmospheric pressure), and yields hydrogen as its principal gaseous product. It seems probable, also, that this same compound is responsible for the hydrocarbons of the paraffin series that make their appearance at low temperatures.

The technical application of our results is readily apparent. In the manufacture of lighting gas there is, as yet, no decided opinion as to the best carbonising temperature to use, nor has the influence that temperature has on the nature and quantity of the products of distillation been thoroughly investigated.

The efficiency of a boiler is largely dependent on the quantity and the nature of those constituents of coal that can be gasified at a comparatively low temperature. The chief loss of efficiency when generating steam by the combustion of coal arises from the cooling effect of the boiler surface on the gases evolved from the coal, whereby their temperature is reduced below the point necessary for complete combustion. According to the nature of the coal, the temperature at which gases can be distilled, and the rate at which the distillation takes place, varies; and the effect of cooling by the boiler surface will also vary with the nature of the gases evolved. It is possible that on the last factor the smoke-producing tendencies of some varieties of coal largely depend.

Previous work of this nature appears to be very scanty, but since this investigation was begun an account has appeared in the technical journals of some work that has been carried out by H. C. Porter and F. K. Ovitz, of the Technological Branch of the United States Geological Survey during 1907-1908 (*J. Gaslighting*, 1908, **107**, 343), which is very similar in character to that described in this part of our work, though done with a different object in view.

Details are given of the distillation at different temperatures of two samples of coal, as follows:

Ziegler Coal, Illinois.

Moisture	7·67	per cent.
Volatile matter	**30·38**	,,
Fixed carbon	**54·32**	,,
Ash	7·63	,,

Retort temperature (°)	500	600	700	800	900	1000	1100
Maximum temperature in coal (°)	390	480	585	685	811	920	1026
Gases evolved from 10 grams (c.c.)	130	535	978	1550	2335	2700	3120
Analysis of Gas.							
CO_2	21·0	6·7	5·7	3·6	2·2	2·5	1·7
"Illuminants"	5·6	4·3	3·6	3·0	3·0	3·6	3·7
CO	**13·3**	**13·9**	**19·1**	**15·7**	**14·5**	**14·4**	**13·9**
H_2	—	14·2	24·1	38·5	48·7	52·6	54·6
CH_4	**16·4**	**34·1**	**30·0**	**27·1**	**20·7**	**18·1**	**18·9**
C_2H_6	14·8	13·6	7·7	5·0	6·0	3·9	4·2
N_2	28·9	13·2	9·8	7·1	4·9	4·9	6·0

Connellsville Coal, Pocahontas.

Moisture	1·10	per cent.
Volatile matter	30·67	,,
Fixed carbon	60·35	,,
Ash	7·88	,,

Retort temperature (°)	500	600	700	800	900	1000	1100
Maximum temperature in coal (°)	390	474	589	705	812	922	1010
Gas evolved from 10 grams (c.c.)	150	625	1220	1723	2080	2900	3530
Analysis of gas.							
CO_2	11·2	3·4	2·7	2·0	1·1	1·1	1·0
"Illuminants"	5·3	5·7	3·8	4·3	4·7	4·3	4·9
CO	5·2	5·3	5·3	7·0	7·2	5·9	7·0
H_2	—	10·9	27·0	38·1	52·0	56·0	58·2
CH_4	4·5	41·2	36·2	36·0	25·2	24·4	21·5
C_2H_6	32·5	18·9	12·9	9·5	7·1	3·0	3·8
N_2	41·3	14·6	12·1	3·1	2·7	5·3	3·6

The "illuminants" are taken to be the benzene and the ethylene hydrocarbons, whilst the figure for ethane includes all higher paraffin hydrocarbons calculated as C_2H_6.

The distillations were conducted in each case on 10 grams of air-dried coal in an atmosphere of nitrogen, which was passed through the retort before heating until the exit gases contained less than 1 per cent. of oxygen.

The most important conclusion drawn by Porter and Ovitz from their work is that the nature of the volatile products distilled from different samples of coal at low temperatures in the early stages of heating varies in accordance with the smoke-producing tendencies of the coal.

They include among the smoke-producing constituents tar, benzene, ethylene, and the higher homologues of methane. From the figures reproduced here it will be seen that the Connellsville yields a larger quantity of these gases than the Ziegler coal at low temperatures, while it is found in practice that there is a greater difficulty in burning coals of the Connellsville type without smoke.

We are inclined to believe that the smoke-producing constituents consist practically entirely of the higher hydrocarbons of the paraffin series; for we have isolated small quantities of propane and butane from the gases evolved from coal at low temperature, and have obtained evidence of the presence of the higher members of the series. These gases readily decompose at temperatures below 600°, depositing carbon; whilst ethylene yields very little carbon on decomposition at this temperature.

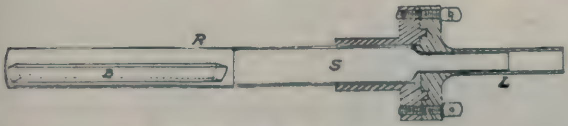
The general trend of the results is in agreement with our own, although it is impossible to make any direct comparison owing to differences in the manner of distillation. We are inclined, however, to doubt the complete absence of hydrogen in the gases distilled at 500°, and we cannot regard the methods of gas analysis employed by Porter and Ovitz as being entirely satisfactory.

EXPERIMENTAL.

The Coal Samples.—The validity of comparison between one distillation and another depends to a very great extent on the obtaining of a uniform and representative sample of coal. The samples were procured in each case by pulverising about 150 kilograms of screened nut coal in a special form of disintegrator, and collecting during the operation about 1 kilogram of the fine dust formed. This dust was then passed through a sieve with 240 meshes per linear inch, and stored in screw-top bottles. About 75 per cent. of the pulverised coal passed through such a mesh.

The Method of Distillation.—Two grams of coal, dried at 107°, are intimately mixed with 3 grams of white sand, which has previously been ignited. The mixture is placed in a thin platinum boat (*B*, Fig. 1) 13 cm. long, which slides easily into a retort, *R*, which consists of a platinum tube 21·5 cm. long and of 1·7 cm. internal diameter.

FIG. 1.



Platinum retort and connexions.

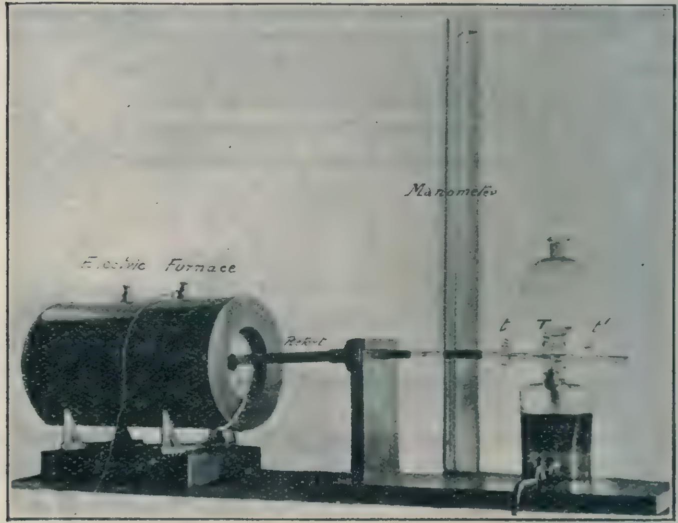
This tube is silver-soldered into a gun-metal collar with a wide flange, whilst a similar flange carrying a short length of gun-metal leading-tube (*L*) of 1 cm. bore is bolted on to the retort by six small screws through the flanges. The face connected with the leading-tube has a projecting ring midway between the centre and the circumference, which is pressed into a corresponding sunk ring on the retort face, using a washer of asbestos and graphite. A perfect vacuum-tight connexion can be made in this manner.

Before this connexion is made, a tar-scrubber (*S*) is fitted into the mouth of the retort. This scrubber consists of a platinum tube packed with ignited asbestos fibre and open at both ends. It is 1·65 cm. in diameter for 8 cm. of its length, and then narrows into a tube 0·8 cm. in diameter and 5·5 cm. long. These dimensions allow of its occupying the position shown in Fig. 1, the wide portion making a good sliding fit inside the retort.

The connexion to the retort having been made, the gun-metal leading-tube is joined by stout rubber pressure tubing to a mercury manometer and a 2-litre gas-holder. The retort and connexions are then exhausted of air through the glass taps t, T, t', the tap t closed, and T, which is a three-way tap, turned so as to make connexion with the gas-holder and the retort as soon as t is opened (Fig. 2).

The whole arrangement is mounted on a wooden support, and runs on wheels so as to allow of the retort being quickly pushed into the furnace, which has been previously brought to the experimental temperature.

FIG. 2.



Distillation apparatus.

As soon as the pressure of the gases evolved is equal to the atmospheric pressure, the tap t is opened, and the gas at once passes into the holder and is collected. Heating is continued for a definite period, usually seventy-five minutes, and the retort then withdrawn and allowed to cool. The gases remaining in the retort are exhausted by means of a mercury pump, and added to the main bulk in the gas-holder. The gun-metal joint is then disconnected, the tar-scrubber and the boat removed and weighed, and the gases analysed.

In this manner the following data are obtained: (1) The rate of evolution of gas; (2) the volume of gas evolved; (3) the composition of this gas; (4) the quantity of tar formed; and (5) the total loss in weight of the coal, that is, the total volatile matter.

The Distillation Furnace.—In order to make sure that the retort shall be heated evenly throughout its length, the tube furnace employed is a platinum-wound electric resistance furnace, which, with a current of a little more than 1 ampere at 200 volts, can attain a temperature of 1400°. The furnace was tested by means of a thermo-couple for each centimetre of its length to make sure that the coal would be in the zone of highest and of uniform temperature when the retort was inserted.

The temperatures are measured by means of a platinum and platinum-rhodium thermo-couple, which runs through the length of the furnace (the junction being in the centre), and is insulated by an unbroken length of silica quill tubing.

The Gas Analyses.—The gases are collected over a mixture of equal parts (by volume) of glycerol and water previously saturated with coal gas. The gases do not dissolve in such a mixture to any appreciable extent, and its use is more convenient than that of mercury.

The gas analyses have been carried out with a modification of the Bone and Wheeler apparatus (*J. Soc. Chem. Ind.*, 1908, **27**, 10). With this apparatus the absorptions are carried out over mercury in one absorption vessel with a comparatively small volume of the particular reagent, which is always used fresh and is at once discarded after use, the absorption vessel being rinsed out with dilute sulphuric acid before the next reagent is used.

The reagents that we have employed for the different constituents are as follows, the absorptions being made in the order named:

Gas.	*Reagent.*
Ammonia	Dilute sulphuric acid (10 per cent.).
Benzene	Concentrated sulphuric acid (D 1·9).
Hydrogen sulphide	Acidified solution of copper sulphate.
Carbon dioxide	Potassium hydroxide solution.
Oxygen	Strongly alkaline pyrogallic acid.
Acetylene	Ammoniacal silver chloride solution.
Ethylene	Bromine water with potassium bromide.
Carbon monoxide	Ammoniacal cuprous chloride solution.

The gas remaining after these absorptions is passed into a set of exhausted glass bulbs containing "oxidised" palladium precipitate heated in a water-bath to 90°. Heating is continued during ten minutes, the bulbs allowed to cool, and the residual gases withdrawn by means of a mercury pump and measured. The change in volume observed is taken to be due to removal of hydrogen by the palladium.

An explosion analysis is then made in the usual manner.

The details of experiments with four samples of coal are given in the tables following.

The distillation temperatures recorded are the retort temperatures, not those existing in the coal. The temperature in the coal itself reaches the retort temperature at the end of two minutes; thus, in a special experiment made to test this point, in which a thermo-couple was embedded in the coal itself, the temperatures recorded immediately after the insertion of the retort in the furnace were as follows:

	Retort.	In coal.
At beginning	830°	400°
After half a minute	790	580
After one minute............	815	780
After one and a-half minutes..	835	835
After two minutes	840	840

The records of the rate of evolution of gas are taken from the moment that the pressure in the apparatus reaches atmospheric pressure. The volumes are not corrected for variation in temperature and pressure.

The total quantity of gas evolved is calculated per gram of ash-free dry coal as "nitrogen-free" gas at 0° and 760 mm.

The different constituents of the gas mixtures are calculated as percentages of the nitrogen-free mixture. From 1 to 4 per cent. of nitrogen is usually found in the mixtures, but since this may partly be due to the presence of traces of air in the retort connexions, or to error in analysis, it is thought best for the purpose of comparison to assume that the gases are free from nitrogen.

The quantities of tarry matter and of total volatile matter are calculated as percentages of the ash-free dry coal.

Coal A (*Bituminous*).

Coal from the Altofts Silkstone Seam. The pulverised nut coal, after passing through a 240-mesh sieve, had the following ultimate analysis:

Carbon	80·50	Per cent. of ash-free dry coal.
Hydrogen	5·45	
Oxygen..................	9·70	
Nitrogen	1·42	
Sulphur	2 93	

and it contained 5·51 per cent. of ash.

Table I.

Rate of Evolution of Gas at Different Temperatures.

Total gas from 2 grams of coal; measured at atmospheric temperature and pressure.

	Distillation temperature.							
	600°	700	750	800	900	1000	1050	1100
	c.c	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
1st minute	40	50	90	145	225	300	375	550 in first three minutes.
2nd ,, ...	25	25	45	75	125	145	90	
3rd ,, ...	15	25	25	35	50	30	25	
4th ,, ...	10	15	15	25	25	25	15	10
5th ,, ...	5	10	10	20	20	5	10	5
Total first 5 minutes..	95	125	185	300	445	505	515	565
Next 5 minutes	22	30	30	60	50	60	25	30
,, 5 ,, ...	13	15	25	25	15	15	15	5
,, 15 ,, ...	25	35	35	27	20	25	15	25
,, 15 ,, ...	15	10	15	13	15	15	15	15
,, 30 ,, ...	10	10	5	10	10	25	15	5

With distillations at 450° and 500°, 25 c.c. and 60 c.c. respectively were evolved, the total duration of heating being two hours.

Table II.

Volatile Constituents Evolved at Different Temperatures.

Per cent. ash-free, dry coal.

Distillation temperature.									
450°	500	600	700	750	800	900	1000	1050	1100
Total volatile matter :									
9·10	18·79	28·37	32·30	34·04	36·30	38·05	38·30	38·80	38·83
Tarry matter :									
4·29	9·05	13·66	14·08	16·20	13·50	12·25	10·40	10·90	9·00

The condensed products at distillation temperatures of 450° and 500° were light-coloured oils.

The coke remaining after all distillations up to and including that at 800° was dull black in colour, and had a tarry odour. Above this temperature the coke was greyish-white and lustrous, and free from any odour of tar.

TABLE III.

Percentage Composition of Gas Evolved at Different Temperatures.

Calculated as "nitrogen-free" gas.

	Distillation temperature.									
	450°	500	600	700	750	800	900	1000	1050	1100
NH_3...	4·70	1·35	1·40	1·60	5·20	1·00	1·00	3·65	3·55	3·00
C_6H_6..	8·60	4·85	5·20	3·40		3·65	3·30			
CO_2....	10·95	3·60	3·50	4·05	3·30	1·70	1·70	1·65	1·65	1·70
C_2H_2..	nil	0·35	—	0·40	—	—	—	0·50	—	nil
C_2H_4..	0·85	1·65	1·80	1·05	0·75	0·90	1·40	1·65	1·55	1·85
CO.....	8·75	6·45	7·10	7·90	9·40	11·85	13·65	15·10	14·80	15·85
H_2	7·00	16·60	26·60	32·70	41·65	48·55	55·70	56·40	56·55	56·65
CH_4...	25·00	37·55	35·20	34·60	29·90	26·10	16·95	17·55	17·05	17·60
C_2H_6..	34·10	27·60	19·20	14·30	9·80	6·25	6·00	3·55	4·85	3·40

TABLE IV.

Total Volume of Gas Evolved per Gram of Ash-free, Dry Coal at Different Temperatures, and Volumes of Principal Constituents.

	Distillation temperature.									
	450°	500	600	700	750	800	900	1000	1050	1100
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
Total gas.	12·00	29·90	99·00	124·00	154·00	218·00	268·0	305·0	315·0	327·0
H_2	0·84	5·00	26·4	40·55	64·20	105·80	149·3	172·0	178·0	185·2
CH_4	3·00	11·25	34·9	42·90	46·05	56·90	45·5	53·5	53·6	57·5
C_2H_6	4·10	8·25	19·0	17·70	15·10	13·30	16·1	10·8	15·3	11·1
CO	1·04	1·95	7·0	9·80	14·45	25·80	36·6	46·0	46·6	51·8
C_2H_4	0·10	0·45	1·7	2·00	1·15	1·95	3·7	5·0	4·9	6·0

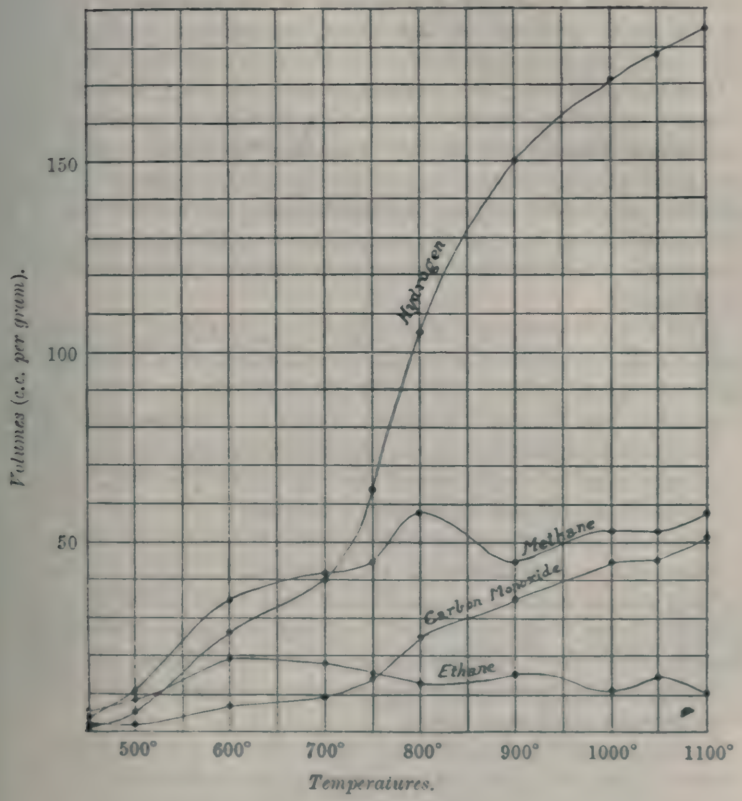
The numbers for hydrogen, methane, ethane, and carbon monoxide are shown graphically in Fig. 3.

All the data obtained indicate that there is a "critical" period in the decomposition of the coal between 700° and 800°. The rate of evolution of gas and the total quantity evolved per gram are nearly double at 800° what they are at 700°; the curve for total volatile matter shows a marked change in character, becoming steeper at the point given by the distillation at 750°; the quantity of tarry products reaches a maximum at 750°; whilst the total quantity of hydrogen evolved is more than doubled between 700° and 800°, the change in the character of the curve being very marked (Fig. 3).

A noteworthy fact regarding the composition of the gases is the presence of a high percentage of ethane in the gases evolved at low temperatures, the percentage decreasing progressively with higher temperatures of distillation.* It will be observed, however, that the actual quantity of ethane varies very little with the temperature of distillation after 600°; and it would appear probable that such quantities as are found to exist in the products of the high-temperature distillations are evolved only during the initial period of slow heating up of the coal which necessarily takes place when the retort is first pushed into the furnace; and that their appearance in the final products is due to their having been swept out of the retort as the rate of evolution of gas increased, and thus

FIG. 3.

COAL *A*.



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[*] It may here be remarked that ethane exists, in quantity up to 5 per cent., in many samples of ordinary lighting gas; a fact which appears to have escaped general notice, and may account, to a certain extent, for the discrepancy so often observed between the calorific value of lighting gas as determined directly and as calculated from analysis.

having escaped decomposition. For, according to Bone and Coward (Trans., 1909, **95**, 1211), the thermal decomposition of ethane is fairly rapid at 675°, and at 1000° it is practically instantaneous.

The greatest interest attaches to the quantities of hydrogen and of methane found in the gases. At a temperature of 750° there is a sudden increase in the total quantity of hydrogen evolved, and the rate of increase is maintained fairly regularly up to 900°.

The question arises as to the nature of the reaction responsible for the evolution of this hydrogen. It cannot be, as has been suggested, that hydrogen is produced at the expense of methane; for the total quantity of the latter gas evolved undergoes very little variation, as is shown in table IV, and graphically in Fig. 3.

It might, however, be contended that the fact that the total quantity of methane evolved undergoes little or no variation after a distillation temperature of 750° has been attained, is due to the fact that, at each of the higher distillation temperatures, a given quantity is evolved during the initial stage of heating up of the coal; and that as soon as the temperature in the coal rises above a certain point, any further methane evolved is at once resolved into its elements.

Bone and Coward have shown (*loc. cit.*, p. 1206), however, that methane is comparatively stable when heated in a porcelain tube at temperatures below 1100°, only about 50 per cent. being decomposed after one minute's heating; whilst at a temperature of 785°—the retort temperature in our experiments corresponding with the maximum rate of evolution of hydrogen—10 per cent. only was decomposed at the end of an hour's heating.

Moreover, the carbon deposited during the course of the thermal decomposition of methane is a characteristic hard and lustrous variety, almost metallic in appearance, and can readily be detected. We have been unable to detect the slightest trace of such carbon deposit below 900° distillation-temperature, although at 1050° a quantity just sufficient to weigh could be brushed off the sides of the platinum boat and retort.

Hydrocarbons of the ethylene series yield a greater quantity of methane than of hydrogen on decomposition below 800°, and in any case the quantity present is insufficient to account for the large increase in hydrogen.

We are inclined to believe that, at a temperature of about 750°, one or more of the higher hydrocarbons of the paraffin series evolved undergoes rapid decomposition, yielding chiefly hydrogen and carbon; decomposition at lower temperatures yielding methane, ethane, and hydrogen. We are studying this point in connexion with another part of this investigation.

Coal C (*Bituminous*).

Coal from Abertillery, South Wales. The pulverised nut coal, after passing through a 240-mesh sieve, had the following ultimate analysis:

Carbon	85·72	Per cent. of ash-free, dry coal
Hydrogen	4·93	
Oxygen	7·34	
Nitrogen	1·09	
Sulphur	0·92	

and contained 7·65 per cent. of ash.

Table I.

Rate of Evolution of Gas at Different Temperatures.

Total gas from 2 grams of coal; measured at atmospheric temperature and pressure.

	Distillation temperature.					
	600°	700	800	900	1000	1100
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
During 1st minute	—	60	100	200	320	475
,, 2nd ,,	—	35	70	105	130	45
,, 3rd ,,	—	25	40	50	25	30
,, 4th ,,	—	20	25	15	15	5
,, 5th ,,	—	10	15	10	10	5
Total first 5 minutes	70	150	250	380	500	560
Next 5 minutes	30	30	50	50	45	40
,, 5 ,,	20	25	50	20	10	5
,, 15 ,,	20	20	30	25	20	15
,, 15 ,,	10	20	20	5	15	5
,, 30 ,,	10	5	15	20	10	5

With a distillation temperature of 500°, 65 c.c. were evolved during two hours.

Table II.

Volatile Constituents Evolved at Different Temperatures.

Per cent. ash-free, dry coal.

	Distillation temperature.						
	500°	600	700	800	900	1000	1100
Total volatile matter	13·40	21·17	25·68	28·96	30·14	31·36	31·50
Tarry matter	7·00	10·02	7·36	10·56	9·67	9·19	8·21

The coke remaining after the distillations at 900°, 1000°, and 1100° was greyish-white and lustrous; that remaining after the distillation at 500°, 600°, 700°, and 800° was dark and compact. This coal does not swell so much on coking as does coal A.

TABLE III.

Percentage Composition of Gas Evolved at Different Temperatures. Calculated as "nitrogen-free" gas.

	Distillation temperature.						
	500°	600	700	800	900	1000	1100
NH_3	2·00	0·70	1·10	0·85	nil	nil	nil
C_6H_6	4·40	3·55	2·40	2·00	1·85	1·45	2·25
CO_2	3·95	3·20	3·40	2·50	1·65	1·20	1·40
C_2H_2	0·45	0·30	0·30	0·05	0·05	0·10	0·50
C_2H_4	0·90	1·05	0·05	0·70	1·05	1·45	1·55
CO	4·70	6·45	7·45	9·80	11·25	13·55	13·00
H_2	8·00	25·05	34·75	50·80	57·05	59·80	60·70
CH_4	64·50	47·20	46·25	28·60	21·80	19·25	18·80
C_2H_6	11·05	12·45	4·25	4·70	5·25	3·10	1·80

TABLE IV.

Total Volume of Gas Evolved per Gram of Ash-free, Dry Coal at Different Temperatures, and Volumes of Principal Constituents.

	Distillation temperature.						
	500°	600	700	800	900	1000	1100
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
Total gas ...	33·50	83·00	135·00	208·00	254·00	296·00	312·00
H_2	2·70	20·80	46·95	105·70	144·95	177·00	189·45
CH_4	21·60	39·20	62·45	59·50	55·50	57·25	58·65
C_2H_6	3·70	10·35	5·75	9·80	13·35	9·15	5·60
CO	1·65	5·35	10·05	20·35	28·55	40·15	40·55

The general behaviour of this coal on heating is similar to that of coal A. This is seen most clearly on comparing curves showing the volumes of the constituent gases evolved at the different temperatures of distillation.

A sudden increase in the quantity of hydrogen evolved is again apparent at a temperature lying between 700° and 800°, whilst the quantity of methane evolved remains remarkably constant at all temperatures above 700°. The presence of "methane-carbon" could only be detected after the distillations at 1000° and 1100°.

The quantity, and the percentage, of ethane evolved is considerably less at all temperatures than in the case of coal A.

Coal D (*Semi-bituminous*).

Coal from Penrhycyber, South Wales. The pulverised nut coal, after passing through a 240-mesh sieve, had the following ultimate analysis:

Carbon	90·72	Per cent. of ash-free, dry coal.
Hydrogen	4·23	
Oxygen	1·25	
Nitrogen	2·99	
Sulphur	0·81	

and it contained 3·5 per cent. of ash.

Table I.

Rate of Evolution of Gas at Different Temperatures.

Total gas from 2 grams of coal; measured at atmospheric temperature and pressure.

	Distillation temperature.				
	700°	800	900	1000	1100
	c.c.	c.c.	c.c.	c.c.	c.c.
During 1st minute	—	90	175	300	550
,, 2nd ,, ...	—	60	120	150	50
,, 3rd ,, ...	—	40	60	25	15
,, 4th ,, ...	—	25	30	25	10
,, 5th ,, ...	—	15	15	10	10
Total first 5 minutes......	100	230	400	510	635
Next 5 minutes...............	25	55	45	40	20
,, 5 ,, ...	20	30	15	10	10
,, 15 ,, ...	20	50	30	10	10
,, 15 ,, ...	10	15	15	5	5
,, 30 ,, ...	10	10	10	5	5

With distillations at 500° and 600°, 30 c.c. and 114 c.c. respectively were evolved, the total duration of heating being two hours.

Table II.

Volatile Constituents Evolved at Different Temperatures.

Per cent. ash-free, dry coal.

	Distillation temperature.						
	500°	600	700	800	900	1000	1100
Total volatile matter	3·54	7·71	10·47	14·40	16·75	17·34	19·00
Tarry matter	0·99	2·10	2·85	2·50	1·73	2·07	not estimated

The coke did not appear to cake at all until a temperature of 800° had been reached; it swelled very little.

Table III.

Percentage Composition of Gas Evolved at Different Temperatures. Calculated as "nitrogen-free" gas.

	Distillation temperature.						
	500°	600	700	800	900	1000	1100
NH_3......	3·10	—	0·80	0·60	0·30	0·20	0·10
C_6H_6......	3·70	1·95	1·40	0·75	0·60	0·70	0·45
H_2S	—	—	0·20	0·35	0·30	0·25	0·25
CO_2	6·85	2·85	1·60	1·40	1·35	1·00	0·20
C_2H_2......	0·05	0·20	0·10	nil	nil	nil	nil
C_2H_4......	0·70	0·90	0·80	nil	0·40	0·25	0·35
CO	4·60	3·95	3·85	6·30	9·30	10·20	11·10
H_2.........	15·70	36·75	43·30	59·65	65·50	69·90	72·90
CH_4	51·50	48·50	45·90	28·35	20·65	14·45	12·85
C_2H_6......	13·70	4·65	2·05	2·50	1·60	2·95	1·80

TABLE IV.

Total Volume of Gas Evolved per Gram of Ash-free, Dry Coal at Different Temperatures, and Volumes of Principal Constituents.

	Distillation temperature.						
	500°	600	700	800	900	1000	1100
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
Total gas ...	13·00	56·00	94·00	193·00	248·00	288·00	333·00
H_2	2·05	20·60	40·70	115·20	162·50	201·30	242·70
CH_4	8·45	27·30	43·20	54·70	51·20	41·60	42·80
C_2H_6	1·80	2·60	2·00	4·80	4·00	8·50	6·00
CO	0·60	2·20	3·60	12·20	23·10	29·40	36·90

Coal B (*Anthracite*).

Coal from Pontyberen, South Wales. The pulverised nut coal, after passing through a 240-mesh sieve, had the following ultimate analysis:

Carbon	92·66	Per cent. of ash-free, dry coal
Hydrogen	3·14	
Oxygen	2·20	
Nitrogen	0·99	
Sulphur	1·01	

and it contained 3·9 per cent. of ash.

TABLE I.

Rate of Evolution of Gas at Different Temperatures.

Total gas from 2 grams of coal; measured at atmospheric temperature and pressure.

	Distillation temperature.				
	700°	800	900	1000	1100
	c.c.	c.c.	c.c.	c.c.	c.c.
During 1st minute	—	50	120	250	375
,, 2nd ,, ...	—	25	95	100	75
,, 3rd ,, ...	—	25	40	25	15
,, 4th ,, ...	—	20	30	20	10
,, 5th ,, ...	—	20	15	10	10
Total first 5 minutes...	15	140	300	405	485
Next 5 minutes............	40	50	43	40	15
,, 5 ,, ...	—	20	10	15	10
,, 15 ,, ...	20	30	20	5	25
,, 30 ,, ...	5	10	5	5	15

With a distillation temperature of 600°, 50 c.c. were evolved during two hours.

FIG. 4.

COALS *D* and *B*.

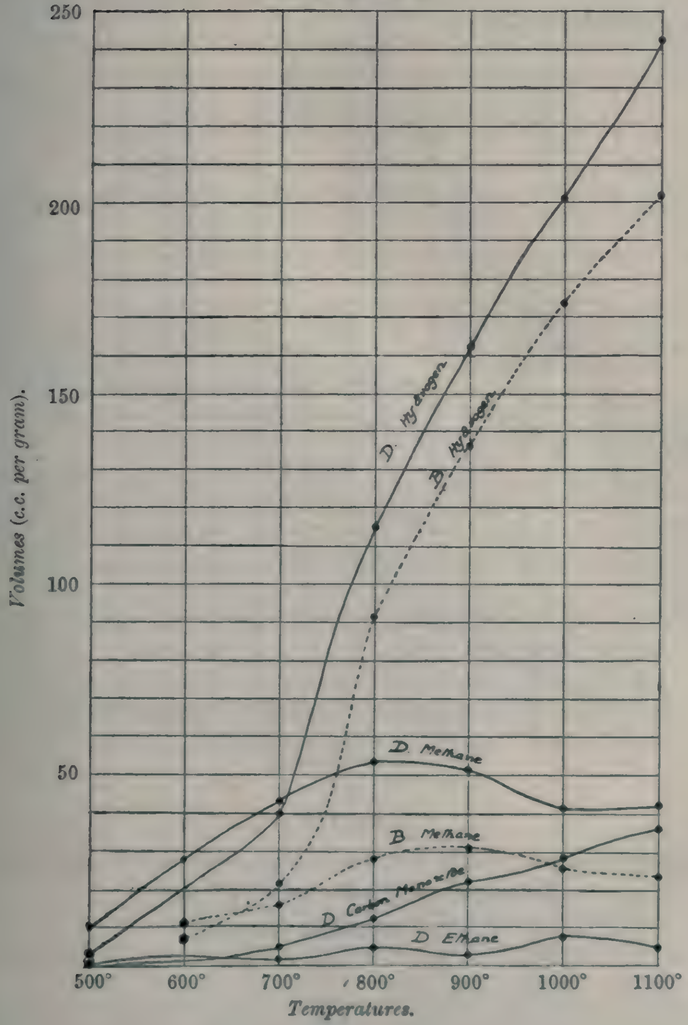


TABLE II.

Volatile Constituents Evolved at Different Temperatures.

Per cent. ash-free, dry coal.

	Distillation temperature.					
	600°	700	800	900	1000	1100
Total volatile matter	3·57	3·76	6·18	7·82	8·77	12·50
Tarry matter	0·22	0·40	0·95	0·80	0·22	not estimate

There was no change in the appearance of the coal after heating except at 1100°, at which temperature some of the particles appeared to have caked slightly.

FIG. 5.

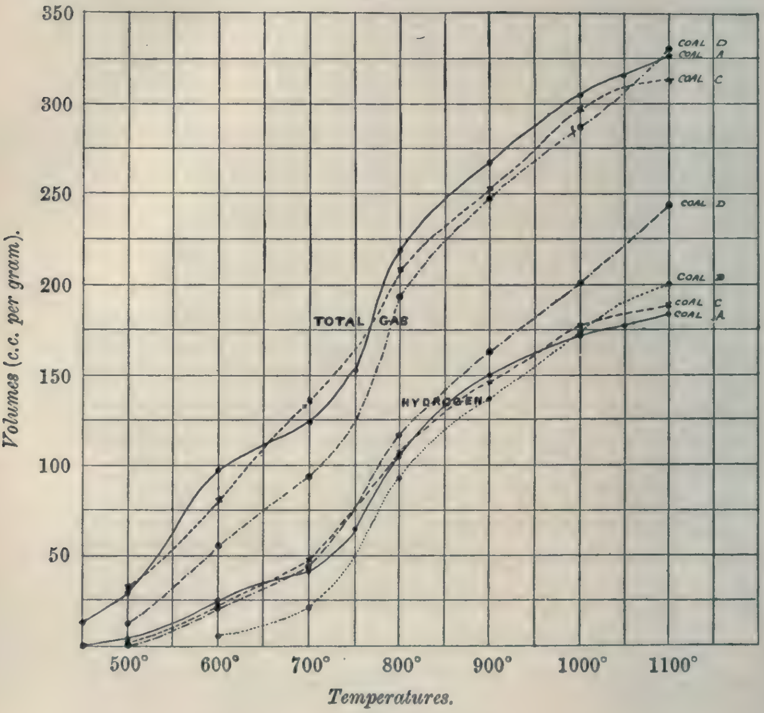


TABLE III.

Percentage Composition of Gas Evolved at Different Temperatures. Calculated as "nitrogen-free" gas.

	Distillation temperature.					
	600°	700	800	900	1000	1100
NH_3	4·35	—	—	—	—	nil
C_6H_6	1·20	2·45	1·35	1·35	1·55	0·75
CO_2	5·55	3·45	1·35	1·55	0·25	1·45
C_2H_2	nil	nil	nil	nil	nil	0·10
C_2H_4	0·10	0·20	nil	0·25	0·25	nil
CO..	6·65	7·85	6·70	9·35	9·70	14·60
H_2	29·35	47·30	68·65	70·50	75·35	74·10
CH_4	51·70	36·60	21·05	15·95	11·40	8·85
C_2H_6	1·00	2·05	0·90	1·05	1·50	0·15

TABLE IV.

Total Volume of Gas Evolved per Gram of Ash-free, Dry Coal at Different Temperatures, and Volumes of Principal Constituents.

	Distillation temperature.					
	600°	700	800	900	1000	1100
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
Total gas	20·5	44·0	133·0	193·0	230·0	272·0
H_2	6·0	20·8	91·3	136·0	173·5	201·5
CH_4	10·6	16·1	28·0	30·8	26·2	24·1
C_2H_6	0·2	0·9	1·2	2·0	3·4	0·4
CO	1·3	3·5	8·9	18·0	22·3	39·8

These two anthracitic coals, D and B, serve to show the difference in behaviour from the bituminous as regards the gases evolved at distillation temperatures above 700°.

There is the same abrupt increase in the quantity of hydrogen evolved between 700° and 800° (Fig. 4), but the rate of increase is maintained up to the highest temperature employed, namely, 1100°, whereas, in the case of bituminous coals, as exemplified by coals A and C, the rate of increase falls off above 900° (Fig. 5).

In the case of coal D (semi-bituminous), the total quantity of gas evolved by distillation at 1100° is greater than in the case of the two bituminous coals, although at 700° it is less. The first products of distillation of the anthracitic coals are probably not such as will allow of the recombination to any great extent of free unsaturated residues to form more complex molecules, as appears to be the case with bituminous coals yielding greater quantities of tarry matter.

ALTOFTS.

CCV.—*The Viscosity of Certain Amides.*

By ALBERT ERNEST DUNSTAN and ALBERT GEORGE MUSSELL.

THE peculiarly constitutive nature of viscosity confers on it considerable value in discriminating between two possible types of structure. The amides may react as though they possessed the formulæ $R{\cdot}CO{\cdot}NH_2$ or $R{\cdot}C\Big<\begin{matrix}OH\\NH\end{matrix}$ (Tafel and Enoch, *Ber.*, 1890, **23**, 1550; Lander, Trans., 1903, **83**, 418), although by comparison with a genuinely hydroxyiminic compound, such as glycolliminohydrin, Hantzsch and Voegelen (*Ber.*, 1901, **34**, 3142) regard $R{\cdot}CO{\cdot}NH_2$ as the correct formulation for the amides. From a physical point of view the amides are undoubtedly associated

(Auwers, *Zeitsch. physikal. Chem.*, 1893, **12**, 689; 1894, **15**, 33; 1897, **23**, 449; 1899, **30**, 521), and the fact that they form additive compounds (Titherley, Trans., 1901, **79**, 413) indicates that the group $\cdot CO \cdot NH_2$ possesses considerable residual affinity. In further support of the usual amidic structure may be cited the work of Hantzsch and Dollfus (*Ber.*, 1902, **35**, 226) and Schmidt (*Ber.*, 1903, **36**, 2459). Fawsitt (*Proc. Roy. Soc. Edin.*, 1904, **25**, 1, 51) found that the fatty amides in aqueous solution were non-electrolytic, and gave normal depression of the freezing point. The same chemist (*Electrochemist and Metallurgist*, 1904, **3**, 664) determined the viscosities of a few amides in aqueous solution, and showed that the viscosity increased with increasing molecular weight.

Meldrum and Turner (Trans., 1908, **93**, 876), in an ebullioscopic examination of a considerable number of amides, found that 90 per cent. of those used were associated in benzene, 80 per cent. in ether, 80 per cent. in chloroform, 10 per cent. in acetone, 45 per cent. in water, and probably 20 per cent. in ethyl alcohol. They connected these results with the dielectric constants of the solvents, and considered that the carbonyl group or the nitrogen atom was the centre of association.

Turner and Merry (Proc., 1910, **26**, 128), using Ramsay and Shields' method, state that all the amides investigated by them are associated.

The object of the present work was to investigate the viscosity of the amides with the view of detecting any hydroxylic nature, for such structure has been found to affect very materially this property in aqueous solution. Again, if the amides possessed the $\cdot C{<}^{OH}_{NH}$ group, then, in pyridine solution, salt formation would probably occur, with enhanced viscosity. Further, the viscosity of the amides in the free condition had not been previously investigated, and it was of interest to determine the equivalent viscosity as being likely to throw light on their relative degrees of association.

EXPERIMENTAL.

The viscosity of a large number of amides, both fatty and aromatic, has been determined for the free substances and for aqueous and pyridine solutions. The materials used were as follows:

Carbamide.—Kahlbaum's purest, m. p. 132°.

Formamide.—Kahlbaum's, redistilled under diminished pressure. 2·916 grams, boiled with alcoholic potash (70 c.c. of 1·155*N*), used, after boiling, 16·25 c.c. of *N*-sulphuric acid, whence $HCO \cdot NH_2 = 99 \cdot 7$ per cent. Boiled with decomposition at 204°/758 mm. (208° corr.); b. p. 141°/65 mm., 136°/50 mm. Brühl

(*Zeitsch. physikal. Chem.*, 1894, **16**, 214) gives b. p. 111—112°/14 mm.

Acetamide.—Kahlbaum's, m. p. 82°, redistilled b. p. 215·5°/749 mm.

Propionamide.—Kahlbaum's, m. p. 80—81°.

n-*Butyramide.*—Kahlbaum's, m. p. 116°.

Thiocarbamide.—Schuchardt's, m. p. 149°, crystallised from water.

Acetanilide.—Prepared from aniline, recrystallised several times from water, m. p. 112°, b. p. 283°.

Benzamide.—Kahlbaum's, recrystallised from hot water, m. p. 128°.

Benzanilide.—Schuchardt's, m. p. 160°, crystallised from alcohol.

Thiocarbanilide.—Schuchardt's, recrystallised twice from alcohol, m. p. 153°.

Methylacetanilide.—Prepared from methylaniline, recrystallised from alcohol, m. p. 101°, b. p. 237°.

Diphenylcarbamide (carbanilide).—Prepared from ketobenzoxazole and aniline, crystallised from much alcohol, m. p. 234° (in sealed tube).

Urethane.—Kahlbaum's, m. p. 51°, b. p. 179°/749 mm.

Cyanuric Acid.—Kahlbaum's, recrystallised from hot water.

Formanilide.—Schuchardt's, recrystallised from hot aqueous alcohol, m. p. 46—47°, b. p. 271°.

Phthalanil.—Schuchardt's, m. p. 205°.

Phthalimide.—Schuchardt's, recrystallised from alcohol, m. p. 230°.

Solvents.—Conductivity water, pyridine partly from Kahlbaum, dried over potassium hydroxide, b. p. 114—116°/742 mm. (corr.), partly from crude coal-tar pyridine fractionated with a long rod-and-disk column, b. p. 116°.

Magnitude of Experimental Error.—Densities were taken in Sprengel pyknometers of 2 c.c. capacity. Two determinations were made, and these usually agreed within a milligram. The density error is not greater than 0·05 per cent. Times of flow were taken until about five concordant results were obtained agreeing within one second; as an example the following may be quoted:

Butyramide, 16·88 per cent. in water.

3′ 27·4″; 3′ 27·4″; 3′ 27·6″; 3′ 27·5″; 3′ 27·7″; 3′ 27·6″. Average = 3′ 27·53″.
Greatest mean error = 0·17 sec.

The viscosity error may be taken as ± 0·1 per cent.

To obtain the equivalent viscosities, two or more determinations were made at different (low) concentrations. A curve was then drawn practically linear near the origin. By arranging the equivalent concentration so low as mol. wt./20, it was possible to interpolate from this linear portion, and so obtain a more correct value than could be observed directly.

The viscosities at high temperatures are not so accurate, since it is very difficult to secure effective thermo-regulation. An example will illustrate the method:

Temperature at start.	Temperature at end.	Time of flow.
104·8°	105·0°	5·28
105·0	103·8	5·31
104·8	104·6	5·27
105·0	105·7	5·27
Average temperature 104·8		Average 5·282

The viscosity error is probably ±0·5 per cent.

The following tables show the results obtained; the figures in the first column representing percentages of the substance in the solvent.

Table I.

Amides in Aqueous Solution at 25°.

(1). *Carbamide*—

	Density.	Viscosity.
1·02	1·000	0·00895
8·13	1·018	0·00939
11·89	1·029	0·00969
15·47	1·033	0·01035
23·12	1·059	0·01088
33·28	1·087	0·01252
38·13	1·102	0·01348
46·18	1·125	0·01561

(2). *Formamide*—

	Density.	Viscosity.
1·70	0·9999	0·00921
40·22	1·054	0·01182
52·2	1·069	0·01283
75·42	1·115	0·02101
79·15	1·118	0·02275
100·0	1·132	0·0331* 0·0326*

(3). *Acetamide*—

	Density.	Viscosity.
0·78	0·9977	0·00890
5·82	1·001	0·00991
17·69	1·008	0·01232
25·95	1·015	0·01458
37·21	1·022	0·01875
69·26	1·038	0·04442

(4). *Propionamide*—

	Density.	Viscosity.
1·245	0·9974	0·00919
5·65	0·9984	0·01025
11·71	1·000	0·01188
22·18	1·005	0·01536
41·48	1·011	0·03030
70·65	1·011	0·05980

(5). n-*Butyramide*—

	Density.	Viscosity.
1·02	0·9972	0·00906
8·11	0·9974	0·01122
16·88	0·9984	0·01458
17·92	0·9987	0·01511

(6). *Formic acid*—

	Density.	Viscosity.
3·05	1·004	0·00907
27·38	1·060	0·01041
73·85	1·161	0·01379
100·0	1·209	0·01580

* From two specimens from Kahlbaum.

Amides in Pyridine Solution at 25°.

	Density.	Viscosity.
Thiocarbamide—		
5·52	0·9949	0·01251
12·57	1·019	0·02019
Acetamide—		
3·87	0·9794	0·00987
16·27	0·9959	0·01381
Benzamide—		
5·16	0·9839	0·01055
12·46	0·9971	0·01331
Benzanilide—		
5·40	0·9839	0·01027
9·02	0·9902	0·01121
12·75	0·9964	0·01252
Thiocarbanilide—		
7·40	0·9919	0·01159
14·51	1·005	0·01416
Methylacetamide—		
6·59	0·9786	0·00967
11·2	0·9819	0·01022
16·44	0·9844	0·01082
Carbanilide—		
5·69	0·9841	0·01045
7·19	0·9862	0·01079
Urethane—		
9·09	0·9832	0·01070
14·96	0·9899	0·01202

	Density.	Viscosity.
Propionamide—		
7·92	0·9769	0·01047
13·66	0·9789	0·01208
23·75	0·9817	0·01615
Cyanuric acid—		
3·20	0·9874	0·01038
Formanilide—		
10·32	0·9903	0·01089
19·14	1·004	0·01335
Phthalanil—		
3·55	0·9821	0·009606
Phthalimide—		
5·05	0·9876	0·009878
11·93	1·006	0·01182
Formamide—		
7·77	0·9871	0·01064
11·10	0·9935	0·01160
17·12	1·0007	0·01365
Acetamide—		
5·65	0·9814	0·01005
8·51	0·9826	0·01088
Carbamide—		
0·91	0·9802	0·00939
Pyridine—*		
100·0	0·9746	0·00884

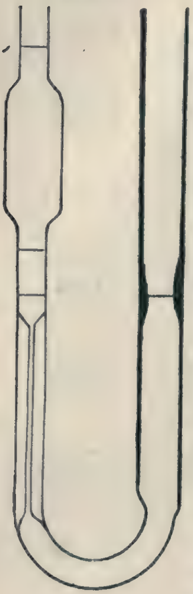
* Hartley, Thomas, and Applebey (Trans., 1908, **93**, 544) give 0·00885.

The Viscosity of the Amides at High Temperatures.

To obtain comparable information as to the relative state of association of the amides, it was necessary to work at somewhat elevated temperatures, seeing that propionamide melts at 81° and acetamide at 82°. A description of the apparatus used may be of interest.

A large beaker filled with cylinder oil of high flash-point was supported on wire gauze and jacketed with asbestos paper, through which two opposite longitudinal slits were cut for observations of the viscometer. Through the metal lid passed a thermometer graduated in fifths of a degree, a stirrer connected with a Henrici motor, and the viscometer. The latter was designed with the view of increased accuracy in filling. The usual method (Ostwald, *Physico-Chemical Measurements*, 1894, 163) is to run in a known volume of liquid from a pipette. This is obviously impossible when working with a substance which is solid at the ordinary temperature, unless the pipette can be kept at a sufficiently high temperature, so that the instrument shown in Fig. 1 was used. It is of the Ostwald type, and merely possesses two etched lines at the same level on the same limb. The viscometer is cleaned and dried, and the compound under observation is distilled into it. Where distillation is impossible, the melted substance must be filtered in. Unless filtration or distillation is resorted to, it is practically impossible to secure freedom from particles of dust, which will inevitably choke the capillary. This is the most fertile source of error in viscometry. The instrument filled just above the marks is placed in the oil-bath, and levelled by means of a gravity bob hung from the supporting clamp. After remaining for ten minutes to attain the bath temperature (a thin flame obtained from a Bunsen burner after unscrewing the chimney, and controlled by a long lever on the tap, gives excellent temperature regulation), the liquid is adjusted to the marks by a capillary pipette, and times of flow are taken and averaged. Absolute densities were measured in a 10 c.c. bottle-shaped pyknometer filled with fused compound. A correction was applied for the known coefficient of expansion of the glass, the volume being determined at 25° and 45° by the water content.

FIG. 1.



The viscometer was calibrated with ethylene dibromide in the following way:

Log viscometer constant = log η – log time – log density.

At 105°, η for ethylene dibromide = 0·00639 (Thorpe and Rodger).

At 120°, η ,, ,, = 0·00562 ,, ,,

Time of flow at 105° = 77·4 secs., and at 120° = 71·9 secs.

Density at 105° = 2·009, and at 120° = 1·979.

whence log $K_{105} = \bar{5}\cdot6138$, and log $K_{120} = \bar{5}\cdot5965$.

Hence the viscosity of a compound at 120° or 105° is obtained from the equation $\eta = K \times \text{time} \times \text{density}$.

The ethylene dibromide used for this purpose boiled at 129·5°/749 mm.

TABLE II.

Amides at High Temperatures.

	η.	*d*.	Mol. wt.	$\eta \times 10^6$/M.V.
105°:				
Formamide............	0·00768	1·061	45	181
Acetamide	0·0132	0·980	59	219
Propionamide	0·0127	0·933	73	162
Urethane	0·00916	1·005	89	103·5
120°:				
Formamide............	0·00659	1·050	45	154
Acetamide	0·0106	0·967	59	174
Propionamide	0·0103	0·925	73	136
Urethane	0·00715	0·991	89	77·8
Formanilide	0·0165	1·076	121	147
Acetanilide............	0·0222	1·034	135	170
Methylacetanilide...	0·00818	0·977	149	53·6

Discussion of Results.

The Amides in Aqueous Solution.

Formamide, acetamide, propionamide, *n*-butyramide; and carbamide were examined in aqueous solution. In Fig. 2 are plotted the viscosity-concentration curves of the above amides, together with those of formic acid and methyl alcohol for comparison.

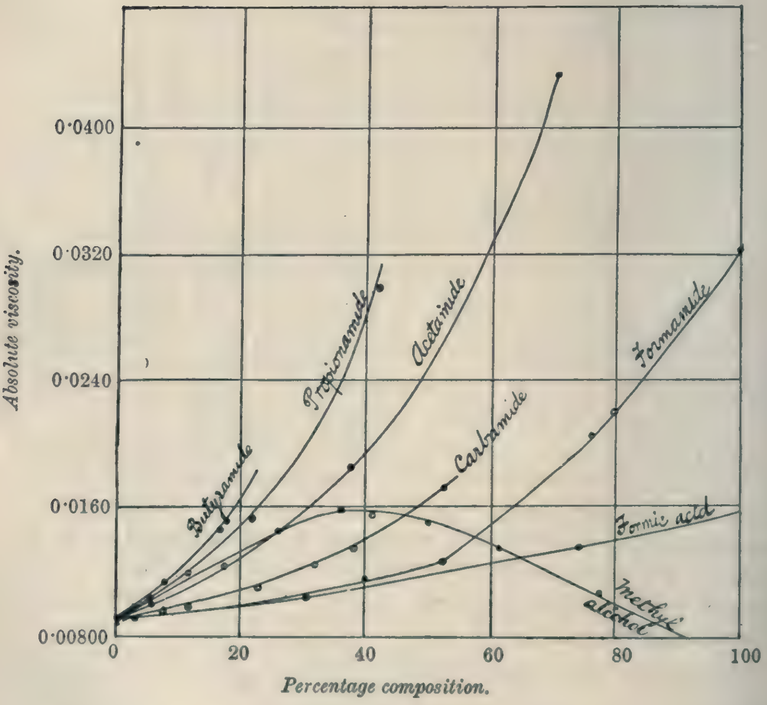
In connexion with formamide, Walden (*Zeitsch. Electrochem.*, 1908, **14**, 718) found a high value for the latent heat of fusion (50·4, acetamide being 69·4). Moreover the expression $\frac{M\lambda\infty}{T_\theta^{\prime}}$ for formamide is 8·31, and for acetamide 11·51, giving the coefficients of association 1·62 formamide, and 1·17 acetamide.

The rapid increase of viscosity with increasing amide concentration is remarkable, and indicate very considerable association on the part of these compounds. Comparing formamide and formic acid, which yield curves of similar type up to a concentration of 30 per cent., it is evident that beyond this limit the formamide curve rises steeply until the relatively high viscosity 0·0326 is reached for the pure substance.

Now it has been shown that the quantity $\frac{\eta}{M.V.} \times 10^6$ has a series constancy; for example, for alkyl chlorides it is 37·4, and for ketones 43·3 (Dunstan and Thole, *J. Chim. Phys.*, 1909, **7**, 204), whilst for associated compounds values in great excess of these are obtained. For formamide, $\frac{\eta \times 10^6}{M.V.} = 682$, and for formic acid this expression = 415. There is thus little doubt that formamide in the free state is extremely associated, and although these numbers do not give an exact value for the degree of association, yet it is possible, qualitatively, to obtain a very fair idea of the relative extents of the molecular complexity. By measuring off the curves, the values of the viscosity coefficients at equimolecular concentrations, the following numbers are obtained:

Mol. wt.	Amide.	Equivalent viscosity at mol. wt./8 per cent.
87	Butyramide	122
73	Propionamide	110
59	Acetamide	102
60	Carbamide	94
45	Formamide	90
46	Formic acid	92
32	Methyl alcohol	99

FIG. 2.

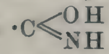


The above equivalent viscosities in aqueous solution illustrate the dissociating action of the solvent. Formamide is almost completely broken down, since its equivalent viscosity is nearly identical with that of formic acid, which does not exist associated with water in aqueous solution. Methyl alcohol, on the other hand, is most probably associated with the solvent. There is a steady increase in viscosity as the molecular weights of the amides become greater. According to Meldrum and Turner (*loc. cit.*), the amides are associated in aqueous solution with the possible exception of carbamide (formamide was not examined by them).

The position of carbamide is interesting, seeing that the curve lies almost exactly midway between those for acetamide and formamide. Although of nearly identical molecular weight, the equivalent viscosity is considerably lower than that of acetamide.

Here, however, another consideration should be advanced. Viscosity is not entirely a matter of molecular mass or molecular volume. What may be termed the molecular shape or symmetry cannot be ignored, and in accordance with this view it is found that the viscosity of *iso*-compounds differs from that of the normal isomerides. It may happen that carbamide is a more symmetrical compound than acetamide, in which case, although the degree of association might be the same, the molecular viscosity would be less.

The Amides in Pyridine Solution.

The choice of pyridine was made in the expectation that if any tendency existed towards the structure  $\cdot\mathrm{C}\Big\langle{}^{\mathrm{OH}}_{\mathrm{NH}}$ on the part of the amides, it would be developed by the well-known basic properties of this solvent. With the possible exceptions of thiocarbamide, cyanuric acid, and thiocarbanilide, this hope was not realised, but at the same time it will be evident from the curve that an approximate separation of the amides in the order of their molecular complexity is achieved. Pyridine is a dissociating solvent (von Laszczynski and von Gorski, *Zeitsch. Elektrochem.*, 1897, **4**, 299), and, like water, tends to break up the aggregates presented to it. It is particularly noteworthy that the amide the molecular viscosity of which was smallest in the fused state, methylacetanilide, affords the curve with the least upward tendency, that is, the least effect on the viscosity of the solvent. For the sake of comparison, viscosities of the solutions have been measured at equivalent concentrations, mol. wt./20 per cent.

The order then becomes:

Mol. wt.	Amide.	At mol. wt /20 per cent.	Mol. wt.	Amide.	At mol. wt./20 per cent.
45	Formamide	0·0093	121	Benzamide	0·0108
59	Acetamide	0·0095	135	Acetanilide	0·0108
149	Methylacetanilide	0·0097	76	Thiocarbamide	0·0109
89	Urethane	0·0097	212	Carbanilide	0·0110
73	Propionamide	0·0097	223	Phthalanil	0·0114
121	Formanilide	0·0098	197	Benzanilide	0·0116
60	Carbamide	0·0101	129	Cyanuric acid	0·0120
123	Phthalimide	0·0102	228	Thiocarbanilide	0·0130

The value for carbamide is not of the same order of accuracy as the other amides, seeing that a concentration of 1 per cent. was the highest obtained. If it be granted that the amides in certain instances do react as acids, then the high molecular viscosities of thiocarbanilide and benzanilide would be explained, and this explanation is at least a possible one. But at the same time the non-acidic nature of the fatty amides is emphasised. The values in pyridine solution are complicated therefore by two causes: (1) the dissociation more or less complete suffered by the dissolved substance; (2) the effect of any acidic nature of the solute. When the equivalent viscosities in pyridine are compared with those in aqueous solution, it is again noticed that formamide has the lowest value; this, of course, may be in each case due to the fact that it is the most easily dissociated, but it must be emphasised once more that the question of molecular symmetry cannot be ignored in drawing comparisons based on viscosity determinations. We intend extending this research to the investigation of the general question of solutions in the amides, and particularly to the question of relative viscosities at corresponding temperatures.

In conclusion, we desire to express our gratitude to Mr. W. E. S. Turner for many useful suggestions and criticism, and to the Research Fund of the Chemical Society for a grant in aid of the work.

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CCVI.—*The Constituents of Leptandra.*

By **Frederick Belding Power** and **Harold Rogerson.**

Under the title of "leptandra," the Pharmacopœia of the United States recognises the dried rhizome and roots of *Veronica virginica*, Linné (*Leptandra virginica*, Nuttall), a plant which is indigenous to the greater part of North America. The above-mentioned underground portion of the plant is used medicinally, and the crude resinous material obtained therefrom is one of the products to which the name "leptandrin" has been assigned.

The first chemical examination of "leptandra" appears to have been that recorded by E. S. Wayne (*Proc. Amer. Pharm. Assoc.*, 1856, p. 34), who stated that, besides essential oil, bitter extractive, tannin, gum, and resin, it contains a crystalline, bitter substance, which separated from the ethereal solution in needles. This substance, although not further characterised, was considered to represent the active principle of the drug, and for it the name "leptandrin" has since been proposed. The same investigator (*Amer. J. Pharm.*, 1859, **31**, 557) also observed the presence of "a saccharine principle having the properties of mannite." It was subsequently indicated by F. F. Mayer (*Amer. J. Pharm.*, 1863, **35**, 298), and more recently by J. U. Lloyd (*Proc. Amer. Pharm. Assoc.*, 1880, **28**, 421), that the bitter principle of the drug is a glucoside, although no definite substance of this class had actually been isolated. Steinmann (*Amer. J. Pharm.*, 1887, **59**, 229) states that he obtained the bitter principle in crystals of a pale lemon-yellow colour, but they yielded no dextrose when boiled with dilute sulphuric acid, and their solution gave no precipitate with the usual alkaloid reagents.

It will be apparent from the brief review of the literature given above that, with the exception of the recorded presence of mannitol, nothing of a very definite nature has up to the present been known respecting the constituents of "leptandra." It was therefore deemed of interest to subject it to a complete examination, and the results are embodied in the present communication.

EXPERIMENTAL.

The material employed for this investigation consisted of a good quality of commercial "leptandra," which conformed in its characters to the description given of the latter in the United States Pharmacopœia.

A small portion (10 grams) of the material was first tested for an alkaloid, but the reactions were so slight as to indicate the presence of not more than traces of such a substance.

Twenty grams of the ground material were successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 35—50°)	extracted	0·11	gram	= 0·55	per cent.
Ether	,,	0·56	,,	= 2·80	,,
Chloroform	,,	1·00	,,	= 5·00	,,
Ethyl acetate	,,	0 65	,,	= 3·25	,,
Alcohol	,,	2·95	,,	= 14·75	,,
	Total	5·27	grams	= 26·35	per cent.

For the purpose of a complete examination, a quantity (55·56 kilograms) of the ground material was extracted by continuous percolation with hot alcohol. After the removal of the greater portion of the alcohol, a viscid, dark-coloured extract was obtained, amounting to 19·79 kilograms.

Distillation of the Extract with Steam. Separation of an Essential Oil.

A quantity (2 kilograms) of the above-mentioned extract was mixed with water, and steam passed through the mixture for several hours. The distillate, which amounted to about 6 litres, contained some oily drops floating on the surface. It was thoroughly extracted with ether, the ethereal liquid being dried and the solvent removed, when 0·9 gram of an essential oil was obtained. The yield of the latter was thus equivalent to 0·16 per cent. of the weight of the drug. This essential oil, when distilled under diminished pressure, passed over between 120° and 160°/25 mm. It was a dark brown, mobile liquid, possessing a strong, persistent odour, and gave no coloration with ferric chloride.

Non-volatile Constituents of the Extract.

After the distillation of the extract with steam, as above described, there remained in the distillation flask a dark-coloured, aqueous liquid (A), and a quantity of a dark brown resin (B). These products, when cold, were separated by filtration, and the resin repeatedly washed with hot water until nothing further was removed, the washings being added to the aqueous liquid.

Examination of the Aqueous Liquid (A).

Isolation of 3 : 4-*Dimethoxycinnamic Acid,* $C_6H_3(OMe)_2{\cdot}CH{:}CH{\cdot}CO_2H$.

The aqueous liquid was repeatedly extracted with ether, and the combined ethereal extracts evaporated to a small volume. On cooling, a quantity (5·0 grams) of a crystalline substance separated. This was removed by filtration, dried, and recrystallised from water, when it separated in yellow needles, melting at about 170°, but after repeated crystallisation from absolute alcohol it was obtained in large, colourless needles, melting at 180—181°. (Found, C = 63·4; H = 5·9; OMe = 29·2. Calc., C = 63·5; H = 5·8; OMe = 29·8 per cent.)

The substance was found to be an acid, and is seen to agree in its characters and composition with 3 : 4-dimethoxycinnamic acid, $C_6H_3(OMe)_2{\cdot}CH{:}CH{\cdot}CO_2H$. When mixed with a portion of the latter, as obtained by the methylation of ferulic acid (Trans., 1907, **91**, 893), the melting point was unchanged. Further confirmation of the identity of the acid was obtained by the preparation of its methyl ester, which separated from absolute alcohol in small prisms, melting at 64°. So far as known to us, this is the first instance in which 3 : 4-dimethoxycinnamic acid has been observed to occur in nature.

The ethereal liquid from which the above-described acid had been separated was diluted somewhat, and then shaken with successive portions of aqueous ammonium carbonate. On acidifying the alkaline liquids, a solid substance was precipitated, which was likewise found to consist of 3 : 4-dimethoxycinnamic acid. The total amount of this acid obtained from 2 kilograms of the original alcoholic extract was 12·0 grams, and was thus equivalent to about 0·2 per cent. of the weight of the drug.

The ethereal liquid was subsequently shaken with a solution of sodium carbonate, which, however, removed nothing. It was then treated with a 10 per cent. solution of sodium hydroxide, when a quantity of resinous material was removed, but from which nothing definite could be isolated. On finally evaporating the ether, only a small amount of a yellow, amorphous product was obtained.

The original aqueous liquid (A), which had been extracted with ether as above described, was thoroughly shaken with successive portions of amyl alcohol. These liquids were then united, washed repeatedly with water, and concentrated under diminished pressure to a small volume, when, on cooling, a considerable quantity of a light brown, amorphous product separated. After removing the amyl alcohol as completely as possible, the entire amount of this product was dissolved in alcohol, and the solution poured into a large volume of water. The precipitate thus produced was collected, washed, and dried, when it could be reduced to a brown powder, but all attempts to obtain it in a crystalline state were unsuccessful. It amounted to 90 grams, or 1·6 per cent. of the weight of drug employed.

The above-described product possessed an intensely bitter and nauseous taste. It was readily soluble in alcohol, but very sparingly so in water, even on boiling. Although the very dilute aqueous solution frothed strongly on agitation, the substance appeared to possess otherwise none of the characters of the saponins, and it was not sternutatory.

In order to obtain some further information respecting the character of the above-described product, a quantity (10 grams) of it was heated with 1000 c.c. of 2 per cent. aqueous sulphuric acid for about four hours, when, on cooling, a hard, black, resinous mass separated. The liquid was then distilled in a current of steam, the distillate extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate. On acidifying the alkaline liquid, again extracting with ether, and removing the solvent, a small amount of an acid was obtained, which, on crystallising from water, separated in leaflets, melting at 131—133°. This acid yielded benzaldehyde on oxidation, and was identified as cinnamic acid. The ethereal liquid which had been extracted with alkali was finally evaporated, but it yielded only a trace of a deep yellow oil.

The aqueous, acid liquid remaining after the distillation with steam, as above described, was separated from the hard, black, resinous mass, which weighed 5·5 grams, and shaken with ether, the ethereal liquid being subsequently extracted with a solution of ammonium carbonate. On acidifying the alkaline liquid, again extracting with ether, and removing the solvent, about 0·3 gram of a crystalline product was obtained, which was found to consist of a mixture of acids. The ethereal liquid which had been extracted with alkali was finally evaporated, but it yielded only a small amount of a yellow oil, which gave a green coloration with ferric chloride.

After extracting the above-mentioned aqueous, acid liquid with ether, it was treated with barium hydroxide for the removal of the sulphuric acid. The filtered liquid readily reduced Fehling's solution, but no crystalline osazone could be prepared from it.

From the above results it was evident that the bitter, amorphous product, which had been obtained by extracting the original aqueous liquid with amyl alcohol, was of a complex nature, and that not more than a small proportion of it could have been glucosidic. It was, moreover, apparent that the acids which it yielded by treatment with dilute sulphuric acid were present in the form of esters, inasmuch as on heating the product with aqueous sodium hydroxide a similar mixture of acids was obtained, and in better yield. This mixture of acids was found on examination to consist chiefly of *p*-methoxycinnamic acid, together with smaller amounts of cinnamic acid and another compound which could not be identified.

The original aqueous liquid, after being extracted with amyl alcohol as above described, was concentrated somewhat, and treated with a slight excess of a solution of basic lead acetate. A copious brown precipitate was thus produced, which was collected, well washed with water, then suspended in water, decomposed by hydrogen sulphide, and the mixture filtered. The filtrate, when concentrated, was dark reddish-brown, and appeared to contain only tannic and colouring matter.

The liquid from the basic lead acetate precipitate was treated with hydrogen sulphide for the removal of the lead, and the filtered liquid concentrated to a small bulk. To the syrup thus obtained a large volume of alcohol was added, when a quantity of a crystalline substance was deposited, which was collected, washed with a little alcohol, and dried. The liquid from which this crystalline substance had been separated was deprived of alcohol, and evaporated to the consistency of a syrup. It evidently contained a large amount of a sugar, since it readily reduced Fehling's solution, and yielded *d*-phenylglucosazone, melting at 209—211°.

Isolation of d-*Mannitol.*

The crystalline substance above described, which amounted to 120 grams, or 2·14 per cent. of the weight of the drug, was recrystallised from alcohol, when it separated in needles, melting at 165—166°, and proved to be *d*-mannitol. (Found, C = 39·5; H = 7·8. Calc., C = 39·6; H = 7·7 per cent.)

Further confirmation of the identity of the above-described substance with mannitol was obtained by the formation of its acetyl and benzoyl derivatives.

On heating a little of the substance with acetic anhydride, a product was obtained which, when crystallised from absolute alcohol, separated in octahedra, melting at 122—124°, and consisted of the hexa-acetyl derivative of mannitol.

Another portion of the substance was benzoylated by the Schotten-Baumann method, as employed by Panormoff (*J. Russ. Phys. Chem. Soc.*, 1891, **23**, 375), when a product was obtained which was soluble in chloroform, but, on the removal of the solvent, formed a syrup. On dissolving this, however, in a small volume of ether, it yielded a mass of needle-shaped crystals, which melted at 149°, and after recrystallisation from a mixture of ethyl acetate and alcohol, or from acetic anhydride, the melting point remained unchanged. (Found, C = 71·3; H = 4·9. Calc., C = 71·4; H = 4·7 per cent.)

This substance is thus seen to be hexabenzoylmannitol, $C_6H_8O_6(CO{\cdot}C_6H_5)_6$, the melting point of which has been given as 149° by Skraup (*Monatsh.*, 1889, **10**, 389) and by Panormoff (*loc. cit.*), but was incorrectly recorded by Stohmann, Rodatz, and Herzberg (*J. pr. Chem.*, 1887, [ii], **36**, 354) as 124—125°.

The optical rotatory power of hexabenzoylmannitol does not appear to have previously been recorded, and this was therefore determined, with the following result:

0·4238, made up to 20 c.c. with chloroform, gave α_D + 2°9′ in a 2-dcm. tube, whence $[\alpha]_D$ + 50·7°.

If the benzoylation of mannitol is conducted in the usual manner, by adding the benzoyl chloride in small quantities at a time, a dibenzoyl derivative, $C_6H_{12}O_6(CO{\cdot}C_6H_5)_2$, is obtained. This is very sparingly soluble in the usual organic solvents, and crystallises in small, prismatic needles, which melt at 178—180°. (Found, C = 61·0; H = 5·8. Calc., C = 61·5; H = 5·6 per cent.)

0·3410, made up to 20 c.c. with pyridine, gave $\alpha_D + 0°22'$ in a 2-dcm. tube, whence $[\alpha]_D + 10·7°$.

Dibenzoylmannitol has previously been obtained by Einhorn and Hollandt (*Annalen*, 1898, **301**, 102), who recorded its melting point as 178°. On adding an excess of benzoyl chloride to a hot solution of mannitol in pyridine, according to the method of the last-mentioned investigators, a crystalline substance began to separate at once, which was evidently the dibenzoyl derivative. When, however, the liquid was heated a little longer, a vigorous reaction ensued, which soon subsided, and a perfectly clear solution was obtained. The product was then poured into water and extracted with ether, when a substance was obtained which melted at 149°, and proved to be hexabenzoylmannitol.

Examination of the Resin (B).

This was a dark brown, brittle mass, and amounted to about 350 grams, being thus equivalent to 6·2 per cent. of the drug. It was dissolved in alcohol, mixed with purified sawdust, and the mixture successively extracted in a Soxhlet apparatus with light petroleum (b. p. 35—50°), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin.

This was a dark brown mass, amounting to 24·5 grams. The extract was dissolved in ether, and the ethereal solution shaken with aqueous ammonium carbonate, which, however, removed only a small amount of resinous material, together with a trace of 3 : 4-dimethoxycinnamic acid. The ethereal solution was then shaken with aqueous potassium carbonate, and the alkaline liquid acidified, when a quantity of black, tarry material was precipitated. This was distilled several times under diminished pressure, when a product was finally obtained which passed over between 220° and 240°/15 mm. as a light yellow oil, and partly solidified on cooling. The free acids thus obtained amounted to 3·7 grams, and were examined together with the combined acids which will subsequently be described.

After treatment with potassium carbonate, as above described, the ethereal solution was shaken with aqueous potassium hydroxide, which, however, removed nothing. On finally evaporating the ether, a residue was obtained, which was hydrolysed by heating with an alcoholic solution of potassium hydroxide. The alcohol was then removed, and the cooled, aqueous, alkaline liquid extracted with ether, the ethereal liquid being dried and the solvent evaporated. On dissolving the residue in alcohol, a small quantity of a solid separated, which, when recrystallised from ethyl acetate, melted at 62—65°, and was found to consist of a hydrocarbon and an alcohol, but the amount was too small to permit of their separation.

Isolation of a Phytosterol, Verosterol, $C_{27}H_{46}O,H_2O$.

The alcoholic filtrate from the above-mentioned solid was concentrated to a small bulk, when, after two or three days, a quantity of a crystalline substance separated. This was collected, washed, and recrystallised from a mixture of ethyl acetate and dilute alcohol, when it separated in flat needles, melting at 135—136°, and gave the colour reactions of the phytosterols:

0·2500, on heating at 110°, lost 0·0126 H_2O. $H_2O = 5·0$.

0·1230 * gave 0·3764 CO_2 and 0·1360 H_2O. $C = 83·5$; $H = 12·3$.

$C_{27}H_{46}O,H_2O$ requires $H_2O = 4·5$ per cent.

$C_{27}H_{46}O$ requires $C = 83·9$; $H = 11·9$ per cent.

A determination of its optical rotatory power gave the following result:

0·2374,* made up to 20 c.c. with chloroform, gave α_D $-0°47'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-33·0°$.

A small amount of the phytosterol was converted into its acetate, which separated from acetic anhydride in flat needles, melting at 119—120°.

The above-described phytosterol evidently represents a member of this class of substances which is widely distributed in nature, and compounds possessing practically the same physical characters have previously been obtained in these laboratories from various sources, such as olive bark, wild cherry bark, and jalap (Trans., 1908, **93**, 909; 1909, **95**, 246; *J. Amer. Chem. Soc.*, 1910, **32**, 87; compare also Menozzi and Moreschi, *Atti R. Accad. Lincei*, 1910, [v], **19**, i, 187). In view of these facts, and in order to distinguish the above-described phytosterol from sitosterol, which differs by the higher melting point of its acetate (*Monatsh.*, 1897, **18**, 551), it would appear desirable to assign to it a specific name. It is therefore proposed to designate it *verosterol*, with reference to the generic name of the plant, *Veronica*, from which it has now been obtained.

Identification of the Fatty Acids.

The alkaline liquid, which had been extracted with ether as above described, was acidified, and the liberated fatty acids collected, dried, and distilled under diminished pressure, when they passed over between 220° and 250°/15 mm. as a pale yellow oil. The acids thus obtained, which amounted to 4·2 grams, were mixed with the previously mentioned portion of acids present in the free state, and the whole converted into their lead salts, the latter being then digested with ether, when a portion was dissolved. Both the soluble and insoluble portions were decomposed by hydrochloric acid, and the regenerated fatty acids purified by distillation under diminished pressure. The soluble portion of the lead salts yielded 4·2 grams of liquid acids, whilst the insoluble portion gave 3·3 grams of solid acids.

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* Anhydrous substance.

The Liquid Acids.—These acids, when distilled under diminished pressure, passed over between 215° and 235°/15 mm. as a yellow oil. An analysis and a determination of the constants gave the following results:

0·1738 gave 0·4842 CO_2 and 0·1788 H_2O. C = 76·0; H = 11·4.

0·3788 absorbed 0·4872 iodine. Iodine value = 128·6.

0·1540 neutralised 0·0307 KOH. Neutralisation value = 199·3.

$C_{18}H_{34}O_2$ requires C = 76·6; H = 12·1 per cent. Iodine value = 90·1; Neutralisation value = 198·9.

$C_{18}H_{32}O_2$ requires C = 77·1; H = 11·4 per cent. Iodine value = 181·4; Neutralisation value = 200·4.

It is evident from the above results that the liquid acids consisted of a mixture of oleic and linolic acids.

The Solid Acids.—These acids, after being again distilled under diminished pressure, were crystallised twice from ethyl acetate, when they melted at 54—56°:

0·1512 gave 0·4190 CO_2 and 0·1728 H_2O. C = 75·6; H = 12·7.

0·2864 neutralised 0·0590 KOH. Neutralisation value = 206.

$C_{16}H_{32}O_2$ requires C = 75·0; H = 12·5 per cent. Neutralisation value = 219·1.

$C_{18}H_{36}O_2$ requires C = 76·1; H = 12·7 per cent. Neutralisation value = 197·5.

These results indicate that the solid acids consisted of a mixture of palmitic and stearic acids in about equal proportions.

Ethereal Extract of the Resin.

During the extraction of the resin with ether a quantity of a sparingly soluble, yellowish-brown substance was deposited, and when the extraction was complete this was collected, washed with ether, and dried, when it was found to weigh 5 grams. It was entirely amorphous, and proved to be similar in character to the product extracted from the original aqueous liquid by amyl alcohol, which has already been described. On heating with aqueous sodium hydroxide, it yielded *p*-methoxycinnamic acid, which was subsequently obtained in larger amount from the chloroform extract of the resin.

The portion of extract which was more readily soluble in ether consisted of a dark resinous mass, amounting to 95 grams. It was thoroughly examined, but nothing except a small quantity of 3: 4-dimethoxycinnamic acid could be isolated from it.

Chloroform Extract of the Resin.

This was a dark-coloured resinous mass, weighing 135 grams. It could easily be reduced to a fine powder, which was tasteless. The chloroform solution of the resin was shaken with aqueous ammonium carbonate, when a small quantity of 3: 4-dimethoxycinnamic acid was removed. The liquid was then shaken with a solution of sodium carbonate, but only a small amount of a resinous product was obtained.

Isolation of p-*Methoxycinnamic Acid*, $OMe\cdot C_6H_4\cdot CH{:}CH\cdot CO_2H$.

After treating the chloroform liquid with the alkaline carbonates, as above described, it was shaken with successive portions of a 10 per cent. solution of sodium hydroxide. These liquids were united and acidified, when a large quantity of a black, resinous product was precipitated. This resinous product was then treated with chloroform, in which it only partly dissolved. The chloroform solution was shaken with aqueous sodium carbonate, and the alkaline liquid acidified, when a crystalline precipitate was obtained. It was thus evident that on shaking the original chloroform liquid with alkali hydroxide, some constituent of it had been hydrolysed. The crystalline precipitate was collected, washed, and dried, when it amounted to 14 grams. By fractional crystallisation from ethyl acetate, it was found to consist of a mixture of 3: 4-dimethoxycinnamic acid and an acid which separated in iridescent, prismatic needles. The latter melted at 170°, assuming a "liquid-crystalline" phase, which persisted until the temperature of 181—182° was reached, when it passed into the ordinary liquid state. The "crystalline" character of the liquid between 170° and 181° was confirmed by observing it through crossed Nicol's prisms. The last-mentioned acid was analysed. (Found, $C=67{\cdot}3$; $H=5{\cdot}8$; $OMe=17{\cdot}3$. Calc., $C=67{\cdot}4$; $H=5{\cdot}6$; $OMe=17{\cdot}4$ per cent.)

In order further to characterise this acid, its methyl ester was prepared. This was accomplished by boiling a solution of the acid in methyl alcohol with a few drops of concentrated sulphuric acid for about two hours on the water-bath. The product so obtained was recrystallised from absolute alcohol, when it separated in flat needles, melting at 88—90°.

The above results render it evident that the substance under examination was *p*-methoxycinnamic acid, which appears only once previously to have been observed to occur in nature. In the form of its ethyl ester, it was found by van Romburgh to be the chief constituent of the essential oil of *Kaempferia galanga*, Linné (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **3**, 38; 1902, **4**, 618; Schimmel's *Bericht*, Oct., 1900, p. 37, and April, 1903, p. 38).

As it appears not to have previously been recorded that *p*-methoxycinnamic acid shows, on heating, a "liquid-crystalline" phase, it was deemed desirable to confirm this observation by means of the synthetically prepared acid. For this purpose a small quantity of *p*-coumaric acid was methylated by means of methyl sulphate, and the product recrystallised from ethyl acetate, when it separated in prismatic needles, melting to the "liquid-crystalline" phase at 170°, and then passing to the ordinary liquid state at 181—182°. A mixture of the naturally-occurring and synthetic acids likewise showed exactly the same behaviour at the same temperatures, and their identity was therefore definitely established.

The chloroform liquid from which the above acids had been isolated was finally evaporated for the removal of the solvent. A resinous product was thus obtained, from which, however, nothing crystalline could be isolated.

Ethyl Acetate and Alcohol Extracts of the Resin.

These extracts were dark, resinous products, amounting to 77·5 and 32·0 grams respectively. They were heated with a 5 per cent. solution of sulphuric acid in aqueous alcohol, but, with the exception of a small quantity of sugar yielding *d*-phenylglucosazone (m. p. 209—210°), nothing definite was obtained.

Summary.

The results of the present investigation may be summarised as follows:

The material employed was commercial "leptandra," consisting of the rhizome and roots of *Veronica virginica*, Linné (*Leptandra virginica*, Nuttall).

An alcoholic extract of this material, when distilled with steam, yielded an amount of essential oil equivalent to 0·16 per cent. of the weight of the drug. This essential oil was a dark brown liquid, which distilled between 120° and 160°/25 mm.

The portion of the extract which was soluble in water contained 3 : 4-dimethoxycinnamic acid, a quantity of mannitol, amounting to 2·14 per cent. of the weight of the drug, and a sugar which yielded *d*-phenylglucosazone (m. p. 209—211°), together with some tannic and colouring matter. It yielded, furthermore, a quantity of a brown, amorphous product, which possessed an intensely bitter, nauseous taste, and amounted to 1·6 per cent. of the weight of the drug. By the hydrolysis of this product there were obtained, besides resinous material, cinnamic and *p*-methoxycinnamic acids.

The portion of the extract which was insoluble in water consisted chiefly of a dark brown resin, which amounted to 6·2 per cent. of the weight of the drug. From this resin the following substances were obtained: A phytosterol, $C_{27}H_{46}O$ (m. p. 135—136°; $[\alpha]_D$ −33·0°), which it is proposed to designate *verosterol*; a mixture of fatty acids, consisting apparently of oleic, linolic, palmitic, and stearic acids; *p*-methoxycinnamic acid, which was present in the form of an ester; and a very small amount of 3 : 4-dimethoxycinnamic acid, which had probably been occluded by the resin.

It has been observed that *p*-methoxycinnamic acid, when melted, passes into a "liquid-crystalline" phase, which persists until a temperature of 181—182° is reached.

It has not been possible to confirm the statement recorded in the literature that "leptandra" contains a crystalline, bitter glucoside, designated as "leptandrin," to which its activity may be attributed. Steinmann (*Amer. J. Pharm.*, 1887, **59**, 229) obtained from "leptandra," in an amount of about 0·1 per cent., a crystalline, yellow substance, which possessed a very bitter taste, and was found not to be a glucoside, although it was not further characterised. From the method by which this substance was isolated, it appears highly probable that it consisted of 3 : 4-dimethoxycinnamic acid, contaminated with a little of the abovementioned, bitter, amorphous product. The fact that an aqueous solution of this product froths strongly on agitation has doubtless led to the statement recorded in the literature that "leptandra" contains saponin.

Some tests with preparations of "leptandra," which were kindly conducted for us by Dr. H. H. Dale, Director of the Wellcome Physiological Research Laboratories, led to the following conclusions.

Both the crude resin and the bitter, amorphous product obtained from the portion of the alcoholic extract which was soluble in water were administered by the mouth to dogs, in doses of 1 gram each, but without any visible effect. The bitter, amorphous product was also tested on the mammal by intravenous injection, and on the isolated mammalian heart, but no characteristic action could be observed. Although the total alcoholic extract of the drug, when given to a dog in doses of 5 grams, produced vomiting, this may be attributed to its nauseous taste and irritant effect on the stomach rather than to any specific action.

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CCVII.—*Aromatic Antimony Compounds. Part I. The Oxidation and Nitration of Triphenylstibine.*

By PERCY MAY.

VARIOUS aromatic derivatives of antimony of the type R_3Sb and R_3SbX_2, in which R represents phenyl, tolyl, anisyl, etc., and X represents Cl, Br, NO_3, or OH, have been prepared by Michaelis and his pupils (Michaelis and Reese, *Annalen*, 1886, **233**, 52; Michaelis and Genzken, *Annalen*, 1887, **242**, 176; Löloff, *Ber.*, 1897, **30**, 2834), but nevertheless far less work has been carried out with these compounds than with the corresponding derivatives of arsenic. Michaelis and Reese showed that the compound $(C_6H_5)_3Sb(OH)_2$ is amphoteric in character, and it therefore appeared to be of interest to observe the effect of the introduction of a nitro-group on the relative stability of the various compounds, such as R_3SbCl_2, $R_3Sb(OH)_2$, $R_3Sb(NO_3)_2$. Michaelis and Reese prepared the compound $(C_6H_5)_3Sb(NO_3)_2$ by the action of nitric acid on triphenylstibine, but if, at the same time, a nitro-group could be introduced into the benzene nuclei, the basicity of the compound $R_3Sb(OH)_2$ might be so depressed that a nitrate such as $R_3Sb(NO_3)_2$ could no longer be formed, and the resulting compound might be of the type $R_3Sb(NO_3)(OH)$.

On nitration, triphenylstibine yields *trinitrotriphenylstibine dihydroxide*, $(C_6H_4{\cdot}NO_2)_3Sb(OH)_2$. It does not appear to be capable of forming a stable sulphate or nitrate, but a *chloride* has been prepared, and it therefore appeared to be desirable to obtain some further information as to the relative stability of the parent substance, $(C_6H_5)_3Sb(OH)_2$, and its salts, and, if possible, to prepare the hitherto unknown normal sulphate, $(C_6H_5)_3SbSO_4$. Triphenylstibine readily reduces concentrated sulphuric acid, with the formation of the desired sulphate, thus:

$$(C_6H_5)_3Sb + 2H_2SO_4 = (C_6H_5)_3SbSO_4 + SO_2 + 2H_2O,$$

and this compound could also be obtained by dissolving the corresponding hydroxide in concentrated sulphuric acid. Dilute sulphuric acid does not attack triphenylstibine, but permanganate and dilute sulphuric acid oxidise it to the hydroxide, $(C_6H_5)_3Sb(OH)_2$. This reaction is of interest from a twofold point of view. On the one hand, it indicates that the sulphate is far less stable than the chloride,* and, on the other hand, it affords fresh evidence of the great stability of the molecule of triphenylstibine as a whole. If alkaline permanganate be used as the oxidising agent, a better yield of the dihydroxide is obtained. Michaelis and Reese state that solutions of this substance in alkali are reprecipitated by mineral acids, but on repeating these experiments it was found that dilute nitric or sulphuric acids produced no precipitate, whilst hydrochloric acid caused precipitation even in very dilute solutions. Probably the experiments of Michaelis and Reese were confined to halogen acids. Similarly, solutions of triphenylstibine sulphate and nitrate in the corresponding concentrated acids can be diluted indefinitely, although these substances themselves are insoluble in dilute acids, but, on addition of dilute hydrochloric acid to their dilute solutions, an immediate precipitate of the chloride is obtained.

The introduction of a nitro-group into the benzene nuclei of the complex $R_3Sb(OH)_2$ not only reduces the salt-forming power of the molecule, but also lowers its stability as a whole. This is shown by the fact that the trinitro-derivative is partly decomposed when boiled with aqueous alkali, yielding a small quantity of nitrobenzene.

EXPERIMENTAL.

The triphenylstibine used in this investigation was prepared by Michaelis and Reese's method, shortened and simplified in some of its details.† The long method of purification after extraction with alcoholic hydrochloric acid, described by these authors, was omitted, the product being instead directly recrystallised from light petroleum. Pure triphenylstibine was thus obtained, the yield being 70 per cent. of the theoretical. The material contained in the petroleum mother liquor was converted into the dichloride, which, after recrystallisation, was still contaminated with traces of an impurity having an extremely irritant action on the mucous membrane. This was finally removed by dissolving the product in concentrated sulphuric acid, pouring the product into aqueous alcohol, and setting aside to crystallise.

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* Triphenylstibine hydroxide combines readily with dilute hydrochloric acid, forming the dichloride.

† A stock solution of dry antimony chloride in dry benzene, made up for these preparations, gradually acquired a deep magenta colour even in the dark.

Nitration of Triphenylstibine and Preparation of Trinitrophenylstibine Dihydroxide, $(C_6H_4{\cdot}NO_2)_3Sb(OH)_2$.

Triphenylstibine was added, in small quantities at a time, to an excess of a mixture of three parts of sulphuric acid and one part of nitric acid, at about 40°. When cold, the mixture was poured into ice-water, the temperature being kept below 25°. The yellow precipitate thus obtained was recrystallised from glacial acetic acid, in which it is very soluble, and separates in flat, transparent, pale yellow crystals, melting at 190—191°. It is also soluble to some extent in alcohol or ether, but does not crystallise well from these solvents. It is insoluble in water, and almost insoluble in benzene, light petroleum, etc.:

Found, $C=41{\cdot}74$; $H=2{\cdot}91$; $N=7{\cdot}79$, $7{\cdot}91$; $Sb=22{\cdot}06$.

$C_{18}H_{14}O_8N_3Sb$ requires $C=41{\cdot}5$; $H=2{\cdot}72$; $N=8{\cdot}07$; $Sb=23{\cdot}11$ per cent.

On treatment with Devarda's alloy no ammonia is evolved. When boiled with glacial acetic acid and zinc dust, or with alcohol, hydrochloric acid, and tin, it yields an easily diazotisable amine, which was not further investigated, as work on this compound is being carried out by Morgan, Micklethwait, and Whitby (Proc., 1910, **26**, 151).

Trinitrophenylstibine Dichloride, $(C_6H_4{\cdot}NO_2)_3SbCl_2$.

This compound is formed, together with the hydroxy-chloride, by boiling trinitrophenylstibine dihydroxide with alcoholic hydrochloric acid. After recrystallising, the product still appeared to be impure, and analysis indicated that it was a mixture of the dichloride and the hydroxy-chloride. The pure dichloride was obtained by the direct nitration of triphenylstibine dichloride, which was dissolved in concentrated sulphuric acid, and then nitrated in the same manner as triphenylstibine. It separates from glacial acetic acid in clusters of small crystals, melting at 157°, which are readily soluble in concentrated nitric acid or glacial acetic acid. As this substance was only obtained in small amount, its properties were not further investigated.

Found, $Cl=12{\cdot}37$.

$C_{18}H_{12}O_6N_3Cl_2Sb$ requires $Cl=12{\cdot}73$ per cent.

Triphenylstibine Sulphate, $(C_6H_5)_3SbSO_4$.

Five grams of triphenylstibine were warmed with an excess of concentrated sulphuric acid on the water-bath. A vigorous reaction suddenly set in, sulphur dioxide being evolved, and a white precipitate formed, which was filtered on asbestos, and washed with cold alcohol, a portion being afterwards extracted with this solvent, in which it is only very sparingly soluble. Small crystals were thus obtained, and similar crystals separated on evaporation of the mother liquor after dilution with water. These crystals melt above 300°, and are soluble in concentrated sulphuric acid, very sparingly so in alcohol, and insoluble in water, dilute sulphuric acid, and most other solvents. The substance is decomposed by warming with aqueous sodium hydroxide, forming sodium sulphate and triphenylstibine hydroxide, the latter dissolving in the excess of alkali:

Found, $S=7{\cdot}30$.

$C_{18}H_{15}O_4SSb$ requires $S=7{\cdot}17$ per cent.

A solution of the sulphate in sulphuric acid may also be obtained by dissolving triphenylstibine hydroxide in the concentrated acid, and this solution, as also the sulphuric acid mother liquor mentioned above, can be largely diluted without any precipitation occurring, but on adding a drop of hydrochloric acid to solutions of any concentration, a precipitate is formed, which, after recrystallisation from alcohol, was found to have the characteristic crystalline form and melting point of triphenylstibine dichloride.

Oxidation of Triphenylstibine with Permanganate.

(1) *In Alkaline Solution.*—Triphenylstibine was boiled for three hours with alkaline permanganate, the manganese dioxide removed, and a portion of the filtrate acidified with hydrochloric acid. A white precipitate was produced, which was recrystallised from alcohol and found to be triphenylstibine dichloride. Another portion of the filtrate was acidified with dilute sulphuric acid, and in this case no precipitate was formed. Evidently the first product of the oxidation is triphenylstibine hydroxide, which dissolves in the alkali, giving solutions from which hydrochloric acid precipitates the chloride, but which are not precipitated by sulphuric or nitric acids.

(2) *In Acid Solution.*—Five grams of triphenylstibine were warmed on the water-bath with an excess of 1 per cent. permanganate and dilute sulphuric acid. The permanganate was gradually decolorised with a slight evolution of carbon dioxide; more permanganate was added from time to time, and finally the precipitate was collected and extracted with alcohol. In this way, a small quantity of a substance was obtained which melted at 210°, contained no sulphur, and appeared to be identical with triphenylstibine hydroxide, as prepared by Michaelis and Reese. This substance was obtained by them in the form of an amorphous powder, but a modification of their method of preparation led to

its being obtained in a well-crystallised state. An alcoholic solution of triphenylstibine dichloride was added to an equal volume of 2*N*-aqueous sodium hydroxide, and the mixture set aside. After some days, triphenylstibine hydroxide crystallised out in beautiful leaflets, which were washed with water and dried. The product was then found to melt at 210°, and resembled the product obtained by Michaelis and Reese in its behaviour towards reagents.

I wish to express my thanks to Sir William Ramsay and to Professor Collie for the interest they have taken in this work, and to the Research Fund Committee of the Chemical Society for a grant towards the expenses thereof.

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LONDON.

CCVIII.—*The Formation of Tolane Derivatives from* p-*Chlorotoluene and* 3 : 4-*Dichlorotoluene.*

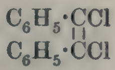
By JAMES KENNER and ERNEST WITHAM.

As is well known, the chlorination of toluene at its boiling point leads to the formation of benzotrichloride. On one occasion, however, Liebermann and Homeyer (*Ber.*, 1879, **12**, 1971), and later Gattermann (*Ber.*, 1884, **17**, 2601), observed the formation of a solid substance as chief product during this reaction, and identified it as tolane tetrachloride, which had previously been obtained by Zinin by the action of phosphorus pentachloride on benzil.

During the preparation of chlorobenzylidene chlorides from *p*-chlorotoluene and 3 : 4-dichlorotoluene, Armstrong and Wynne similarly obtained products which were identified as di- and tetrachloro-tolane tetrachlorides. The present authors have also had the same experience in preparing *p*-chlorobenzotrichloride from *p*-chlorotoluene, but, in common with earlier investigators of this reaction, they have failed to find a clue to the conditions which lead to the formation of the tolane derivative.

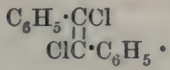
Liebermann and Homeyer (*loc. cit.*), it is true, attributed the condensation to sulphuric acid which had been carried over into the mixture, but in the case of the authors' experiments such an explanation is improbable, as the gas, after being passed through sulphuric acid, was led through a tube packed with asbestos, and, moreover, the introduction of sulphuric acid into the boiling chlorotoluene has not been found to initiate the condensation.

This is the more unfortunate as the only other general method of preparing tolane tetrachloride and its derivatives is that used first by Hanhart (*Ber.*, 1882, **15**, 899), which consists in the removal of chlorine from benzotrichloride by the action of copper powder, and does not give satisfactory results, either as regards yield or purity of product. Hanhart, apparently unable to isolate any definite substance from the tarry product, had recourse to distillation, and obtained the two forms of tolane dichloride, now recognised as the stereoisomerides:



$$\begin{array}{l} C_6H_5\cdot CCl \\ \qquad\;\, \| \\ C_6H_5\cdot CCl \end{array}$$

and



$$\begin{array}{l} C_6H_5\cdot CCl \\ \qquad\;\, \| \\ \qquad ClC\cdot C_6H_5 \end{array}$$

Onufrowicz (*Ber.*, 1884, **17**, 833), who succeeded in isolating the tetrachloride, showed at the same time that it could be converted into *cis*-tolane dichloride by distillation, thus explaining Hanhart's result.

Later, Fox (*Ber.*, 1893, **26**, 653), without reference to Onufrowicz's paper, carried out the same reaction with *o*-chlorobenzotrichloride, and distilled the product, obtaining the *cis*- and *trans*-2 : 2′-dichlorotolane dichlorides. The authors have repeated Fox's work in the hope of separating the tetrachloride, but have been unable to find any evidence of its production, and, as recorded on p. 1966, succeeded, as he did, in isolating only the dichlorides.

As *p*-chlorobenzotrichloride, unlike the *o*-derivative, forms the tetrachloride, which can be isolated without difficulty, the opportunity was taken of testing the applicability of the decomposition observed by Onufrowicz to substituted tolane tetrachlorides. As was expected, 4 : 4′-dichlorotolane tetrachloride, when distilled, behaves in a precisely similar manner to tolane tetrachloride, and yields the *cis*-form of the dichloride.

Further, the tetrachloride was submitted to reduction, and results of some interest were obtained. Zinin (*Ber.*, 1871, **4**, 289) showed that the action of zinc on alcoholic solutions of tolane tetrachloride led to the formation of the stereoisomeric dichlorides. Liebermann and Homeyer (*Ber.*, 1879, **12**, 1971) used zinc dust in place of zinc, and obtained the same products, whilst Lachowicz (*Ber.*, 1884, **17**, 1165) subsequently arrived at the same result by reducing a boiling concentrated acetic acid solution with iron filings. Wislicenus and Blank (*Annalen*, 1888, **248**, 1) repeated Zinin's work, and Eiloart (*Amer. Chem. J.*, 1890, **12**, 239), who studied the two dichlorides from the stereochemical point of view, upheld the opinion already expressed by Wislicenus (*loc. cit.*), that the less soluble isomeride, with the higher melting point, was the *cis*-form, although it may be remarked that this is contrary to the usual rule.

The reduction products obtained from 4 : 4′-dichlorotolane tetrachloride in alcoholic solution by means of zinc dust vary according to the temperature employed. If conducted at 50°, the products are the two 4 : 4′-dichlorotolane dichlorides, which respectively melt at 166—167° and 86—87°, and, in addition, 4 : 4′-dichlorotolane; but if carried out at the boiling point of the alcoholic solution, the isomeride melting at 166—167° can no longer be found, the reduction products being the dichloride of lower melting point and 4 : 4′-dichlorotolane.

If the conclusions drawn by Wislicenus and Blank respecting the *cis*- and *trans*-isomerism of the tolane dichlorides can be accepted, then it will follow by analogy that the dichlorotolane dichloride, melting at 166—167°, will be the *cis*-form. The entire absence of this isomeride from the reduction product obtained by working at the higher temperature, and the evidence that, unlike the dichloride (m. p. 86—87°), it is readily reduced may perhaps be regarded as supporting this view.

As already mentioned, tolane tetrachloride was originally obtained by Zinin by the action of phosphorus pentachloride on benzil, and this would doubtless provide a general method of preparation were it not that, as is well known, the isolation of the benzoins which should furnish the benzils on oxidation has been accomplished only in a few instances. Especially is this the case where negatively substituted aldehydes are submitted to the benzoin reaction. The authors hoped to use *o*-chlorobenzaldehyde as the starting point for the preparation of the 2 : 2′-dichlorotolane tetrachloride, which could not be isolated in the experiments already mentioned, but found that when the benzoin condensation was attempted, *o*-chlorobenzoic acid was the chief product. Greater success attended experiments with *p*-chlorobenzaldehyde, for although the product of the benzoin condensation was a resinous mass from which the pure substance could not be isolated, oxidation with nitric acid led to the production of the 4 : 4′-dichlorobenzil, identical with the substance obtained by hydrolysing 4 : 4′-dichlorotolane tetrachloride with acetic acid by Liebermann and Homeyer's method.

It has not hitherto been possible to apply the reaction to the preparation of 2 : 2′-dichlorobenzil, because the attempt to prepare 2 : 2′-dichlorotolane tetrachloride by the chlorination of the *cis*-dichloride merely led to the conversion of the greater part into the more stable *trans*-form. Chlorine is known to be a particularly effective agent for the interconversion of stereoisomerides. Liebermann and Homeyer (*loc. cit.*) confirmed Limpricht's statement that the tolane dichlorides were stable towards acetic acid, and the present authors found the same to hold good for the 2: 2′-dichlorotolane dichlorides.

Experimental.[*]

Armstrong and Wynne (*private communication*), in the preparation of *p*-chlorobenzylidene chloride from *p*-chlorotoluene, employed chlorine prepared from manganese dioxide and hydrochloric acid, washed by passage through water, and dried over sulphuric acid. For each of seven operations, 126 grams of *p*-chlorotoluene were used, and it was found that in the first two only a very small quantity, but in the last five, considerable amounts, of 4: 4′-dichlorotolane tetrachloride separated in a crystalline form on cooling. The rate at which the chlorine was absorbed did not seem to influence the tolane condensation: thus, in the first two and the last two operations the figures for increase in weight due to chlorination and, in brackets, the duration in hours were 74 (16), 71 (15), 70 (14), 67 (16)—the calculated increase in weight being 69 grams.

The present authors have used liquid chlorine obtained from Kahlbaum as the source of the gas, and have passed the chlorine through sulphuric acid (to allow of the rate being checked) and asbestos wool before introducing it into the boiling *p*-chlorotoluene. With one exception they have been unsuccessful in obtaining the 4: 4′-dichlorotolane tetrachloride. Throughout, they have chlorinated to the stage of *p*-chlorobenzotrichloride, and the usual daily increase in weight was 15 grams, but on the one occasion when the tetrachloride was formed, 44 grams on the first day, and 22 on the second, were taken up. The yield of the tetrachloride from 100 grams of *p*-chlorotoluene was 44 grams, and the mother liquor consisted of *p*-chlorobenzotrichloride. All attempts to repeat the conditions leading to the formation of the tolane derivative have been unsuccessful.

4: 4′-*Dichlorotolane tetrachloride*, $C_6H_4Cl{\cdot}CCl_2{\cdot}CCl_2{\cdot}C_6H_4Cl$, crystallises from chloroform in thin, well-defined, flat plates. It melts at 190°, and dissolves only sparingly in alcohol, but readily in chloroform, benzene, or light petroleum:

(P) 0·5923 gave 0·9367 CO_2 and 0·1212 H_2O. C=43·13; H=2·27.
0·327 „ 0·7216 AgCl. Cl=54·58.
$C_{14}H_8Cl_6$ requires C=43·19; H=2·06; Cl=54·75 per cent.

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[*] The study of 4: 4′-dichlorotolane tetrachloride was begun by Mr. S. Parrish, B.Sc., at the Royal College of Science. He examined its reduction products, obtaining the *cis*- and *trans*-4: 4′-dichlorotolane dichlorides, and prepared from it 4: 4′-dichlorobenzil and the corresponding hydrazone. Unfortunately, he was unable to complete the work, and the investigation has been taken up afresh by the present authors. Analyses prefixed by the letter P were made by Mr. Parrish.—W. P. W.

3 : 4 : 3′ : 4′-*Tetrachlorotolane tetrachloride*,

$C_6H_3Cl_2 \cdot CCl_2 \cdot CCl_2 \cdot C_6H_3Cl_2$,

is formed when 3 : 4-dichlorotoluene is chlorinated to the stage of 3 : 4-dichlorobenzylidene chloride under conditions such that sulphuric acid used as drying agent could not be carried forward mechanically (Armstrong and Wynne, *private communication*). The tetrachloride in this case did not separate on cooling, but was isolated by extraction with chloroform from the semi-solid residue left after fractionation of the 3 : 4-dichlorobenzylidene chloride (b. p. 274—275°). It crystallises from chloroform in small, diamond-shaped plates, which melt at 197°:

0·1214 gave 0·3037 AgCl. Cl = 61·88.

$C_{14}H_6Cl_8$ requires Cl = 61·97 per cent.

4 : 4′-*Dichlorotolane Tetrachloride from* p-*Chlorobenzotrichloride.*

To prepare the tetrachloride, *p*-chlorobenzotrichloride (40 grams), benzene (60 grams), and copper powder (30 grams) were boiled in a reflux apparatus for about six hours until the reaction seemed to be complete. The hot solution, freed from copper powder by filtration, deposited crystals of the tetrachloride and of *p*-chlorobenzoic acid, the latter of which was removed by extraction with sodium carbonate solution. The yield of tetrachloride from 207 grams of the trichloride amounted to 110 grams.

On crystallisation from chloroform, it was obtained in plates identical in appearance, melting point (190°), and composition (Cl = 54·58 per cent.) with the product formed during the chlorination of boiling *p*-chlorotoluene.

When heated at 230°, the tetrachloride decomposes with the elimination of hydrogen chloride, and at a higher temperature, about 270°, chlorine also can be detected in the escaping gas. This decomposition was studied more closely by distilling 5 grams of the tetrachloride under a pressure of 90—130 mm. The first portion of the distillate was a colourless liquid, which passed over at 234°, but the remainder was solid, and, when crystallised from acetone, formed small, rhombic crystals, which melted at 166—167°. This crystalline compound was subsequently identified as cis-4 : 4′-*dichlorotolane dichloride* (p. 1965):

0·192 gave 0·3712 CO_2 and 0·045 H_2O. C = 52·72; H = 2·60.

$C_{14}H_8Cl_4$ requires C = 52·85; H = 2·54 per cent.

Reduction of 4 : 4′-*Dichlorotolane Tetrachloride.*

The reduction was carried out by suspending the tetrachloride (5 grams) in boiling absolute alcohol (500 c.c.), and adding gradually during two days zinc dust (4 grams) and glacial acetic acid (30 c.c.). The solution, freed from zinc dust by filtration, deposited, on cooling, very thin, nacreous flakes, amounting in all to 1·5 grams. On analysis, this proved to be 4 : 4′-dichlorotolane.

Concentration of the alcoholic filtrate to 150 c.c. furnished material amounting in all to 1·2 grams, which consisted of long, slender, brittle, prismatic needles, and was identified as *trans*-4 : 4′-dichlorotolane dichloride. Further concentration gave only small, ill-defined separations, mixed with zinc acetate.

By carrying out the reduction at 50°, instead of at the boiling point, a third substance, crystallising in lustrous, thin, diamond-shaped plates, was obtained in addition to the other two. It was identified as *cis*-4 : 4′-dichlorotolane dichloride, but no estimate could be formed of the relative proportion of the two isomerides in the reduction product.

cis-4 : 4′-*Dichlorotolane dichloride*, $C_6H_4Cl\cdot CCl\colon CCl\cdot C_6H_4Cl$, is less soluble in alcohol than the *trans*-isomeride. It melts at 166—167°:

(P) 0·1710 gave 0·3087 AgCl. Cl = 44·66.

$C_{14}H_8Cl_4$ requires Cl = 44·62 per cent.

When reduced in boiling alcoholic solution with zinc dust and acetic acid, it yields 4 : 4′-dichlorotolane.

trans-4 : 4′-*Dichlorotolane dichloride* dissolves readily in alcohol, and separates from solution in characteristic, prismatic needles. It melts at 86—87°:

(P) 0·354 gave 0·6808 CO_2 and 0·0861 H_2O. C = 52·45 ; H = 2·70.
0·3347 „ 0·5986 AgCl. Cl = 44·25.

$C_{14}H_8Cl_4$ requires C = 52·83 ; H = 2·52 ; Cl = 44·65 per cent.

4 : 4′-*Dichlorotolane*, $C_6H_4Cl\cdot C\vdots C\cdot C_6H_4Cl$, is much less soluble in alcohol than the two dichlorides, and appears to be dimorphous, as it crystallises from solution sometimes in nacreous flakes, and sometimes in slender needles. Usually it melts at 175—176°, but on one occasion the melting point first observed was 153—154°, which, after solidification of the specimen and re-fusion, rose to and remained constant at 175—176°. On analysis of two different preparations:

(i) 0·1626 gave 0·4064 CO_2 and 0·0518 H_2O. C = 68·16 ; H = 3·54.
(ii) 0·1710 „ 0·4262 CO_2 „ 0·0458 H_2O. C = 67·97 ; H = 2·97.
(i) 0·3517 „ 0·4080 AgCl. Cl = 28·70.

$C_{14}H_8Cl_2$ requires C = 68·02 ; H = 3·26 ; Cl = 28·72 per cent.
$C_{14}H_{10}Cl_2$ „ C = 67·47 ; H = 4·05 ; Cl = 28·48 „

These analyses point to the tolane formula, but the production of a tolane, rather than a stilbene or dibenzyl derivative, by reduction of the dichlorotolane tetrachloride seemed sufficiently remarkable to require confirmation. Accordingly, chlorine was passed through a solution of the compound in chloroform until no more of the gas was taken up, and, after removal of the solvent, it was found that the product consisted of 4 : 4′-dichlorotolane tetrachloride in practically quantitative amount. Hence the conclusion is drawn that the reduction product is, as stated, 4 : 4′-dichlorotolane.

The formation of a tetrachloride during the preparation of *o*-chlorobenzotrichloride from *o*-chlorotoluene was not observed, and as attempts to make 2 : 2′-dichlorobenzil, which would have furnished a means of obtaining it, were unsuccessful, recourse was had to Fox's process in the hope that it might be isolated from the product of the action of copper powder on *o*-chlorobenzotrichloride.

Treatment of o-*Chlorobenzotrichloride with Copper Powder.*

o-Chlorobenzotrichloride (20 grams) was dissolved in benzene (30 grams), and heated with copper powder (15 grams) for twenty-five hours in a reflux apparatus. After filtration, repeated extraction of the residue with benzene, and removal of the benzene by distillation, the residue was allowed to dry on a porous plate for a fortnight.

In spite of many attempts with different solvents, it was not found possible to extract from this residue any substance other than *o*-chlorobenzoic acid (m. p. 136°). As a similar residue from benzotrichloride, when heated at 200° with 80 per cent. acetic acid, gave a relatively large yield of benzil, a portion of this viscid substance was also heated with acetic acid, but furnished only *o*-chlorobenzoic acid. Yet when the part which had not gone into solution in the acetic acid was dried and distilled, it gave both *cis*- and *trans*-2 : 2′-dichlorotolane dichlorides. It is difficult to resist the conclusion that the tetrachloride is not formed in the condensation, or, if formed, suffers decomposition into the dichlorides under the conditions of the experiment, being less stable than the 4 : 4′-dichlorotolane tetrachloride, which requires to be heated at above 200° before decomposition into the dichloride takes place.

To confirm Fox's results (*loc. vit.*), a portion of the viscid product was distilled under 11 mm. pressure. Below 210° the distillate was colourless, and solidified on cooling. By crystallisation from light petroleum, it was separated into two portions, the one consisting of clusters of radiate needles, melting at 136°, identical with *o*-chlorobenzoic acid, and the other of prismatic crystals, melting at 172—173°, which proved to be *cis*-2 : 2′-dichlorotolane dichloride (Cl = 44·73 per cent.). The later distillate was brown, and, after purification, consisted for the most part of the *cis*-dichloride, whilst the residue in the flask, when extracted by light petroleum, yielded large, transparent rhombs, melting at 127—128°, which agreed in properties with the description given of *trans*-2 : 2′-dichlorotolane dichloride (Cl = 44·5 per cent.).

When the *cis*-2 : 2′-dichlorotolane dichloride is reduced in boiling alcoholic solution with zinc dust and acetic acid under the conditions already described for the 4 : 4′-isomeride, it is converted into 2 : 2′-dichlorotolane (m. p. 87°). The same substance is also formed when the dichloride is heated with copper powder at 260°.

4 : 4′-*Dichlorobenzil.*—When 4 : 4′-dichlorotolane tetrachloride is heated with glacial acetic acid (40 c.c.) and water (10 c.c.) at 170° for six hours, it is converted into 4 : 4′-dichlorobenzil, which separates in the tube in long, slender, yellow needles, and when recrystallised from alcohol was found to melt at 193°. Montagne (*Rec. trav. chim.*, 1902, [ii], **21**, 19) gives the melting point as 200°:

(P) 0·3735 gave 0·8162 CO_2 and 0·1039 H_2O. C = 59·60 ; H = 3·09.
(P) 0·2318 „ 0·2305 AgCl. Cl = 25·59.
$C_{14}H_8O_2Cl_2$ requires C = 60·22 ; H = 2·89 ; Cl = 25·42 per cent.

Hantzsch and Glover obtained this compound from the corresponding benzoin, which was formed from *p*-chlorobenzaldehyde by the benzoin condensation (*Ber.*, 1907, **40**, 1519). The quantities of materials used and the exact conditions are not given by them, and it may be of interest to note that while studying the benzoin condensation some years ago, Miss E. S. Hooper, B.Sc., failed to isolate the benzoin from this source, although the product, when oxidised by nitric acid, gave a 40 per cent. yield of 4 : 4′-dichlorobenzil (m. p. 191°), which was identical with that obtained from 4 : 4′-dichlorotolane tetrachloride (*private communication*).

The *monohydrazone*, $C_6H_4Cl\cdot C(:N\cdot NH\cdot C_6H_5)\cdot CO\cdot C_6H_4Cl$, crystallises from alcohol in small, yellow prisms, and melts at 178°:

(P) 0·0965 gave 6·4 c.c. N_2 (moist) at 20·5° and 758 mm. N = 7·52.
$C_{20}H_{14}ON_2Cl_2$ requires N = 7·59 per cent.

The authors wish to express their thanks to Professor Wynne, who directed their attention to this problem, and has given them much valuable assistance and advice during its investigation.

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CCIX.—*Some Reactions of Keten. Combination with Hydrocyanic Acid.*

By Stella Deakin and Norman Thomas Mortimer Wilsmore.

In a note published by Miss F. Chick and one of us (Proc., 1908, **24**, 77), it was stated, among other things, that keten combined with liquid hydrogen chloride under pressure at the ordinary temperature to form acetyl chloride:

$$CH_2{:}CO + HCl = CH_3{\cdot}COCl,$$

there being no evidence of the formation of the isomeric chloroacetaldehyde or of its condensation product, dichloroethyl acetate. Under similar conditions keten also combined with hydrogen sulphide, forming acetyl sulphide, the so-called thioacetic anhydride: *

$$2CH_2{:}CO + H_2S = (CH_3{\cdot}CO)_2S.$$

Finally, it was mentioned that keten reacted with hydrocyanic acid, but that the product was not, as might have been anticipated, acetyl cyanide or pyruvonitrile.

The reaction between keten and hydrocyanic acid has now been further investigated, and a new compound, liquid at the ordinary temperature, has been isolated in a pure state. The actual constitution of this compound has, however, not yet been elucidated; but, as our collaboration has come to an end, and as the substance in question has somewhat remarkable properties, we venture to place on record the results so far obtained.

Analysis and molecular weight, the latter having been found both by the vapour density and the cryoscopic methods, showed the substance to have the empirical formula $C_5H_5O_2N$, its formation taking place according to the equation:

$$2CH_2{:}CO + HCN = C_5H_5O_2N.$$

The difficulty in the way of determining its constitution lies in its instability in presence of reagents. For, although it has a boiling point of 173°, and its vapour does not dissociate at the temperature of boiling aniline, it behaves in all the reactions hitherto studied as if it were merely a mixture of keten and hydrocyanic acid, were it not that the velocity of reaction is slower.

Thus with water, either alone or in the presence of acids or alkalis, acetic and hydrocyanic acids are slowly formed:

$$C_5H_5O_2N + 2H_2O = 2CH_3{\cdot}CO_2H + HCN.$$

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* In the note referred to there is a misprint, the b.p. of the acetyl sulphide obtained being given as 55—58° instead of 155—158°.

Alcohol in presence of a trace of mineral acid acts in a similar way, giving ethyl acetate and hydrocyanic acid:

$$C_5H_5O_2N + 2C_2H_5{\cdot}OH = 2CH_3{\cdot}CO_2{\cdot}C_2H_5 + HCN.$$

With aniline a violent reaction takes place, acetanilide and hydrocyanic acid being produced:

$$C_5H_5O_2N + 2C_6H_5{\cdot}NH_2 = 2CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_5 + HCN.$$

Saturation of an ethereal solution of the substance with hydrogen chloride at a low temperature, followed by cautious addition of water, gave only ammonium chloride together with acetic and formic acids, and an attempt to reduce it by means of hydrogen in presence of platinum black led to no definite result. Obviously therefore the substance is not a derivative of *cyclo*butan-1 : 3-dione.

Although we have no very definite experimental evidence to offer in support of it, still we may perhaps be allowed to hazard a guess as to the constitution and mode of formation of the new compound. We may suppose that hydrocyanic acid combines in the first place with a portion of the keten in a way similar to its reaction with aldehydes and ketones to form a cyanohydrin, which in this case would be the nitrile of the unstable α-hydroxyacrylic acid:

$$CH_2{:}CO + HCN = CH_2{:}C(OH){\cdot}CN.$$

As this nitrile contains a hydroxyl group, the latter would at once react with more keten to form the corresponding acetate:

$$CH_2{:}C(OH){\cdot}CN + CH_2{:}CO = CH_2{:}C(OAc){\cdot}CN.$$

It may be objected to this hypothesis that α-hydroxyacrylonitrile would change, at least in part, into the well-known isomeric acetyl cyanide or pyruvonitrile, which should accordingly be found among the products of the reaction. It may well be, however, that at the temperature of the experiment this intramolecular change is comparatively slow, whereas the reaction between keten and hydroxyl is practically instantaneous. A second necessary condition is that the combination of hydrocyanic acid with keten shall be slow, otherwise, with excess of hydrocyanic acid present, there would be no keten available for the second stage of the process. That this condition was fulfilled in our experiments was shown by the fact that a large part of the keten had time to polymerise to *cyclo*butan-1 : 3-dione, although hydrocyanic acid was present in considerable excess. Following out the hypothesis, the decomposition with water may be supposed to proceed thus:

$$\begin{aligned} &CH_2{:}C(CN){\cdot}O{\cdot}CO{\cdot}CH_3 + H_2O \\ &\qquad = CH_2{:}C(OH){\cdot}O{\cdot}CO{\cdot}CH_3 + HCN \\ &\qquad = (CH_3{\cdot}CO)_2O + HCN. \\ &\qquad (CH_3{\cdot}CO)_2O + H_2O = 2CH_3{\cdot}CO_2H. \end{aligned}$$

The reaction with aniline may take place as follows:

$$\begin{aligned}&CH_2{:}C(CN){\cdot}O{\cdot}CO{\cdot}CH_3 + C_6H_5{\cdot}NH_2\\ &\qquad = CH_2{:}C(CN){\cdot}OH + CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_5\\ &\qquad = CH_3{\cdot}CO{\cdot}CN + CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_5.\end{aligned}$$

$$CH_3{\cdot}CO{\cdot}CN + C_6H_5{\cdot}NH_2 = CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_5 + HCN.$$

The reaction with alcohol is less easy to follow, especially as it requires the presence of mineral acid. It may be mentioned that the structure suggested is consistent with the molecular volume, refractivity, and dispersion of the substance.

The actions of Grignard's reagent and of nitrosyl chloride on keten have also been studied. In both cases the keten condensed for the most part to brown, resinous substances, but from the reaction with Grignard's reagent a small quantity of acetone was obtained, probably formed thus:

$$CH_2{:}CO \longrightarrow CH_2{:}C(OMgI){\cdot}CH_3 \longrightarrow CH_2{:}C(OH){\cdot}CH_3 \longrightarrow CH_3{\cdot}CO{\cdot}CH_3.$$

It was thought that nitrosyl chloride might give nitrosoacetyl chloride or the isomeric oximinoacetyl chloride, but the only substance that could be isolated in a pure state was chloroacetyl chloride.

EXPERIMENTAL.

Preparation of Keten and of the Hydrocyanic Acid Derivative.

The pyrogenic method of preparing keten, previously described by one of us (Trans., 1907, **91**, 1938), has been somewhat improved. Spiral condensers provided with a cylindrical bulb at the lower end are now used in place of the simpler pattern previously illustrated, and it has been found advisable to insert a second trap between the generator and the main condenser. Any keten which condenses in the traps can be readily distilled over into the main condenser at the end of the operation. The main condenser is kept at $-110°$ to $-120°$ by means of a bath of alcohol and ether cooled by suitable addition of liquid air, which is not poured into the bath itself, but into a kind of flattened, metallic test-tube suspended from the top of the Dewar vessel. At a lower temperature the spiral of the condenser becomes rapidly blocked with crystals, while at a higher temperature the condensation of the keten is incomplete, owing to its dilution with other gases. A platinum wire of about 0·2 mm. diameter and 5 cm. free length has been found to give the best results. With a longer or thicker wire some keten will be carried away by the increased rush of gas, as the wire must be kept nearly at its melting point in any case. A current of about 7 amperes is used to commence with, but this must be gradually raised to 12 or 14 amperes as the reaction proceeds, as the wire becomes coated with a layer of conducting carbon. The acetic anhydride is added in charges of about 50 grams, a clean wire being used for each fresh charge. By carefully removing the layer of carbon by crushing it with pliers, one wire may sometimes be made to serve for three charges before breaking. After heating for about an hour and a-half, about half of the acetic anhydride will have disappeared, and the remainder will have become dark brown. The reaction is then stopped, the spent charge is removed, a clean wire is inserted, and a fresh charge of acetic anhydride is poured in. Including subsidiary operations, three or four such charges can be run through in a day, yielding altogether 15 to 20 c.c. of crude keten. The acetic anhydride should be as pure as possible, or the yield will be much reduced; but inferior samples may be greatly improved in this respect by previously distilling from phosphoric oxide. Keten may also be prepared from acetone, but is then very impure. Strange to say, glacial acetic acid appears to be quite unacted on by the hot wire.

To prepare the hydrocyanic acid derivative, 15 to 20 c.c. of keten were distilled into an exhausted bomb-tube cooled in liquid air. About twice this quantity of anhydrous hydrocyanic acid was added, and the tube was then sealed off before the blowpipe. The hydrocyanic acid was prepared by the action of 50 per cent. sulphuric acid on potassium cyanide, and was dried by passing it through a long column of calcium chloride. It was stored in a bulb provided with two taps, from which it could be distilled into the bomb tubes as required. As there was an interval of only about 10° between the melting point of the hydrocyanic acid and the temperature at which the keten began rapidly to polymerise, arrangements had to be made to keep the keten cold until the hydrocyanic acid had melted, and then to mix the two liquids as rapidly as possible. Accordingly, on removing the bomb tube from the liquid air, the lower end containing the keten was well jacketed in wool, the upper part containing the hydrocyanic acid being left exposed to the air, and the tube was placed in an inclined position in a shaking machine and shaken for about two hours, or until it had attained the temperature of the room. It was then placed in an ice-safe until wanted. Since considerable pressure was necessarily developed in the tubes as the temperature rose, to minimise the effects of a possible explosion, the shaking and removal to the ice-safe were attended to by one of us at times when the laboratory was otherwise unoccupied. The contents of the tubes were only slightly coloured brown, showing that much less brown resin had been formed than when keten polymerises in the ordinary way. Before opening, the tubes were again cooled to −78°, when, as the contents had solidified, they could be opened with impunity, and they were then removed from the bath and allowed to attain the temperature of the room. As the contents showed the marked tendency to bump characteristic of hydrocyanic acid, a capillary tube connected with a source of dry hydrogen was passed down to the bottom of the bomb-tube as soon as the contents were sufficiently melted. With the help of the current of hydrogen, most of the hydrocyanic acid was then distilled off, the tube being finally warmed to about 50° in a water-bath. The contents of three such tubes were fractionally distilled under 100 mm. pressure, a Claisen flask being employed, to the second neck of which a Young's "pear" still-head with four bulbs had been sealed. The liquid separated mainly into two fractions, one boiling at about 70—80°, which was chiefly *cyclo*butan-1 : 3-dione, and the other boiling at 100—110°, which contained the bulk of the new substance. Some brown residue was left in the flask, and crystals of dehydracetic acid, which were identified in the usual way, and which were due to the polymerisation of *cyclo*butan-1 : 3-dione, were deposited in the neck of the flask and lower portion of the still-head. After repeated fractionation of the portion of higher boiling point, 7 grams of a colourless liquid were obtained, which boiled constantly at 110·0—110·4°/100 mm. (corr.), this being the yield from about 50 c.c. of crude keten. The fractionation was carried out in dry hydrogen. Carbon dioxide was unsuitable for this purpose, as it was very soluble in the liquid.

Composition and Properties of the Hydrocyanic Acid Derivative.

The carbon and hydrogen were determined by the method previously used for "acetylketen" (Trans., 1908, **63**, 947). Attempts to estimate the nitrogen by the Kjeldahl method were unsuccessful owing to loss of hydrocyanic acid, and a modification of the Dumas method was therefore employed. The substance was weighed in an exhausted thin-walled glass bulb, the weight of the air removed from the bulb (0·66 c.c. = 0·8 milligram) being added to the apparent weight of the substance. The bulb was packed in copper oxide in the combustion tube, and, when all the air in the latter had been swept out with carbon dioxide, it was broken by means of a pointed glass rod attached to the inlet tube. The vapour density was determined by the Hofmann method, using freshly distilled aniline in the outer jacket. The volume observed was corrected for the gas and vapour driven off from the walls of the endiometer, and, in measuring the pressure, allowance was made for the temperature of the mercury column and for the vapour pressure of mercury at 184°, the boiling point of aniline under 756·7 mm. pressure. The volume remained constant for about half an hour, showing that the vapour of the substance was stable at the temperature of boiling aniline. The benzene used in determining the molecular weight by the cryoscopic method had been previously distilled from sodium:

0·1705 gave 0·3393 CO_2 and 0·0672 H_2O. C = 54·2; H = 4·4.
0·1369 „ 0·2702 CO_2 „ 0·0580 H_2O. C = 53·8; H = 4·7.
0·1999 „ 21·7 c.c. N_2 (dry) at 14·8° and 755·1 mm. N = 12·8.
0·0859 „ 58·6 c.c. at 184° and 375·9 mm. M.W. = 111·2.
0·0882, in 16·93 benzene, gave $\Delta t = -0{\cdot}260^\circ$. M.W. = 100·2.
0·0697, „ 16·93 „ „ $\Delta t = -0{\cdot}186^\circ$. M.W. = 110·8.
0·1157, „ 16·93 „ „ $\Delta t = -0{\cdot}298^\circ$. M.W. = 114·8.
$C_5H_5O_2N$ requires C = 54·1; H = 4·5; N = 12·6 per cent.
M.W. = 111·04.

Under 772 mm. pressure, the liquid boiled at 173° (corr.), but it began to turn brown a little below that temperature. On cooling, a white opalescence appeared at about −45°, which disappeared again on warming to −42°, but this must have been due to a trace of moisture or other impurity, as the substance remained liquid, although it became very viscous, down to −78°. On cooling with liquid air, it froze to a white solid, which melted at −196° to −195°. Owing to the presence of the opalescence, the melting point could not be found by visual observation, but it was readily determined by means of a thin wire, moisture being excluded by jacketing the wire with calcium chloride in the upper part of the tube. On repeated trials, the wire was found to be immovable up to −196°, but it could be moved up and down at −195°.

The density was determined at various temperatures. Two samples of the substance were used, the first of which had been distilled some weeks, and the second a few days before the experiment. The densities in each series lie very nearly on a straight line, but there is a difference of about five parts in 10,000 between the two series. As a mean of four weighings, the pyknometer contained 0·74325 gram of water weighed in air at 18°. The temperatures in the table have been corrected to the hydrogen scale:

	Weight of substance in air.		${}_4\delta_t$.	
t.	I.	II.	I.	II.
9·3°		0·7997		1·0746
10·0	0·7995		1·0743	
13·9		0·7960		1·0695
14·2	0·7961		1·0697	
16·6		0·7937		1·0664
18·5	0·7925		1·0647	
21·3		0·7901		1·0614
22·9	0·7889		1·0598	
24·8		0·7870		1·0571
29·9	0·7833		1·0521	
30·3		0·7826		1·0511

Taking the mean of the two series by graphic interpolation, the density of the liquid between 10° and 30° is given by the equation:

$$_4\delta_t = 1{\cdot}0685 - 0{\cdot}00112\ (t - 15°).$$

Consequently, assuming the molecular weight to be 111·04, the molecular volume at 15° is 103·9, whereas the molecular volume calculated for the formula $CH_2{:}C(CN){\cdot}O{\cdot}CO{\cdot}CH_3$ from Traube's values for the atomic volumes (Traube, *Grundriss der physikalischen Chemie*, 1904, p. 120; Smiles, *Chemical Constitution and Physical Properties*, 1910, p. 125) is 100·2.

The refractive indices of the same two samples were measured by means of the Pulfrich refractometer. The densities were obtained by interpolation from the values given above, the two series being kept separate:

Line.	Sample.	t.	$_4\delta_t$.	N.	M.R.
C.	I.	16·9°	1·0667	1·42443	26·580
C.	II.	22·6	1·0598	1·42150	26·598
D.	I.	16·0	1·0676	1·42771	26·734
D.	II.	23·1	1·0592	1·42435	26·771
G'.	II.	22·5	1·0599	1·43756	27·478

Taking the mean of the two series, and using the values for the atomic refractivities and dispersions given in Landolt and Börnstein's "*Tabellen*," we obtain the following values for the molecular refractivity and dispersion:

	C	*D*	*G'* – *C*
Found	26·59	26·75	0·89
Calculated for $CH_2{:}C(CN){\cdot}O{\cdot}CO{\cdot}CH_3$	26·34	26·49	0·79

At the ordinary temperature the hydrocyanic derivative is a colourless, somewhat oily liquid. It has a rather pleasant, although slightly pungent odour, resembling that of the nitriles. It is readily miscible with all the ordinary organic solvents, but is sparingly soluble in cold water. It is more readily soluble in hot water, separating again as an emulsion on cooling. It is, however, slowly decomposed and dissolved by water on keeping, even in the cold, acetic and hydrocyanic acids being formed, and this whether the aqueous solution was originally neutral, acid or alkaline; but on warming it with aqueous alkalis or sodium carbonate, some brown substance is also formed. This hydrolysis has been studied quantitatively in both acid and neutral solution. Since methyl-orange cannot be used as an indicator for acetic acid, and phenolphthalein is useless in presence of soluble cyanides, the following method of titration was adopted. Standard alkali free from carbonate was first added in slight excess, that is, in the proportion of rather more than three equivalents of alkali to one molecule of the substance, and the cyanide was titrated with standard silver nitrate, the end-point being shown, as usual, by the formation of a permanent opalescence. A second equal volume of silver solution was then added, in order to replace all the CN' in solution by NO_3', after which the excess of alkali could be found by means of standard acid and phenolphthalein. Proceeding in this way, the alkali used corresponded with the hydrocyanic as well as with the acetic acid, so that, to find the amount of the latter, the hydrocyanic acid as found from the silver titration had to be subtracted from the total acid. To carry out the hydrolysis in acid solution, a weighed amount of the substance was placed in a stoppered flask, together with 50 c.c. of water and 1 c.c. of 0·1092*N*-sulphuric acid. The mixture was kept overnight, warmed for a few minutes on the water-bath, cooled, and titrated, the sulphuric acid being allowed for. The silver nitrate was 0·1*N*, and the alkali 0·1055*N*:

0·3041 required 13·33 c.c. silver and 76·91 c.c. alkali; or 1 mol. gave 0·973 mol. HCN and 1·988 mol. $C_2H_4O_2$.

0·2943 required 12·90 c.c. silver and 72·69 c.c. alkali; or 1 mol. gave 0·973 mol. HCN and 1·919 mol. $C_2H_4O_2$.

For the hydrolysis in alkaline solution, the substance was added at once to excess of the standard alkali. After about two hours at the ordinary temperature, the reaction appeared to be complete, and the solution was titrated:

0·2820 required 12·16 c.c. silver and 70·85 c.c. alkali; or 1 mol. gave 0·967 mol. HCN and 1·975 mol. $C_2H_4O_2$.

0·3142 required 13·86 c.c. silver and 80·80 c.c. alkali; or 1 mol. gave 0·979 mol. HCN and 2·032 mol. $C_2H_4O_2$.

The reaction is thus not quite quantitative, but it is sufficiently so to prove the validity of the equation given on p. 1968.

An attempt was next made to hydrolyse the CN group without breaking up the molecule. 2·33 Grams of the compound were dissolved in about 20 c.c. of dry ether; the solution was cooled to −78°, and dry hydrogen chloride was passed in until two layers began to separate, the lower one being a solution of ether in liquid hydrogen chloride. Two molecular proportions of water, dissolved in 20 c.c. of ether and cooled to −78°, were then added, and the mixture was kept overnight, the temperature gradually rising to about 0°. As no reaction appeared to have taken place, even on warming to the boiling point of ether, a third molecular proportion of water was added, and ether was evaporated until water began to separate. On again keeping overnight at the ordinary temperature, ammonium chloride crystallised out, and the solution was then fractionally distilled. After the ether had been expelled, a fraction passed over at 85—103°, which gave all the reactions of formic acid. A second fraction, which passed over at 103—135°, was also acid. It was redistilled from concentrated sulphuric acid to destroy any formic acid, and it then answered to the tests for acetic acid. A small quantity of liquid which still remained in the flask was heated under a pressure of 35 mm. to 230°, but it merely charred without distilling. The hydrolysis of the hydrocyanic acid derivative had therefore followed practically the same course as in aqueous solution.

The substance did not appear to react with absolute alcohol, but on adding dry hydrogen chloride the odour of ethyl acetate was noticed. On treating another portion of the alcoholic solution with lime, a vigorous reaction took place, hydrocyanic acid and ethyl acetate being given off. To a larger portion of the solution a small quantity of ethylsulphuric acid was added, and the mixture was left for two days, when hydrocyanic acid and ethyl acetate were again noticeable. On passing a current of dry air through the solution and then into water, hydrocyanic acid was readily identified in the latter. The alcoholic solution was then boiled for some time over phosphoric oxide in a flask fitted with a reflux condenser, and finally distilled, when, after all the hydrocyanic acid had been driven off, a sample of ethyl acetate was obtained, which boiled steadily at 77° (corr.).

The compound reacted vigorously with aniline, hydrocyanic acid being given off, and a solid substance being formed, which proved to be acetanilide, melting at 113° (corr.). This was confirmed by taking a mixed melting point with a sample of pure acetanilide from other sources. The reaction appeared to be quantitative.

Action of Grignard's Reagent on Keten.

The reagent (magnesium methyl iodide) in dilute ethereal solution was cooled to −50°, and gaseous keten was slowly passed in. A very vigorous reaction took place, and much heat was evolved, as was shown by the amount of solid carbon dioxide which was required to maintain the low temperature. As only resinous substances appeared to be formed, the experiment was repeated, but this time the keten was largely diluted with dry hydrogen, the dilution being effected by passing the hydrogen through liquid keten at −78° to −70°. The ethereal solution became dark reddish-brown and very viscous, and a yellow, resinous solid separated. The mixture was decomposed with powdered ice, and the magnesium hydroxide was dissolved by addition of dilute hydrochloric acid, leaving a considerable amount of brown resin, which was not soluble in either the water or the ether. This was removed by filtration, and the filtrate was fractionally distilled. After the ether had been removed, a small quantity of liquid passed over at about

100°, which had a strong odour of acetone. The presence of acetone was confirmed by the iodoform reaction, by the alkaline mercuric chloride and nitroprusside tests, and by the formation with benzaldehyde of distyryl ketone (m. p. 111—112°, corr.). No other compound could be isolated.

Action of Nitrosyl Chloride on Keten.

The nitrosyl chloride was prepared by passing nitric oxide into liquid chlorine at about $-60°$ until saturated. The chlorine was obtained from hydrochloric acid and potassium permanganate. It was washed with water and dried with sulphuric acid. The nitric oxide was produced by the action of nitric acid on copper, and was purified by passing first through 50 per cent. potassium hydroxide solution and then through concentrated sulphuric acid. The nitrosyl chloride was fractionally distilled before use to remove any excess of chlorine.

At first, attempts were made to carry out the reaction by condensing the keten with excess of nitrosyl chloride in bomb-tubes by means of liquid air, and allowing the temperature gradually to rise, but violent explosions took place as soon as the nitrosyl chloride melted. Accordingly, another method was tried, gaseous keten being passed slowly into excess of nitrosyl chloride at a temperature just above the melting point of the latter ($-61°$). Vigorous reaction took place at once, with evolution of much heat, hydrogen chloride and an odour of carbonyl chloride being given off, and a white solid separating out, which melted at about $-50°$. If the temperature was allowed to rise during the reaction, much gas was evolved, which, on analysis, proved to be a mixture of hydrogen chloride, carbonyl chloride, carbon dioxide, acetylene, and nitrogen. The acetylene and some or all of the carbon dioxide were impurities in the original keten. The gas did not contain nitric oxide. After all the keten had been added, the temperature was allowed to rise, and a current of hydrogen was passed through the mixture in order to remove the excess of nitrosyl chloride, when a dark brown, very viscous liquid was left. On distilling this under a pressure of 95 to 100 mm., a colourless liquid passed over at 58—68°. This liquid did not contain nitrogen. Under atmospheric pressure it boiled at 106°. It reacted with water to form chloroacetic acid, and with aniline it gave chloroacetanilide, melting at 133°, which was confirmed by taking a mixed melting point with a sample of chloroacetanilide from another source. The colourless liquid was therefore chloroacetyl chloride, in the formation of which the nitrosyl chloride had apparently acted merely as a source of chlorine. A large quantity of a brown, resinous substance was left in the distilling flask. This was found to contain nitrogen, but a definite compound could not be obtained from it. Attempts to obtain a clean reaction by previously diluting the nitrosyl chloride with dry ether met with no better success.

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CCX.—*The Polymerisation of Keten.* cyclo*Butan*-1 : 3-*dione* ("*Acetylketen*").

By FRANCES CHICK and NORMAN THOMAS MORTIMER WILSMORE.

IN a previous paper (Trans., 1908, **93**, 946) we stated that when keten, either in the liquid or the gaseous state, is left to itself at the ordinary temperature, a brown substance is formed, the chief constituent of which is a colourless liquid of a very pungent odour, boiling at 126—127°/760 mm. (corr.), and which, after having been frozen, melts at $-7°$ to $-6°$; and we showed by combustion analyses, by determination of the vapour density according to the Hofmann method, and by measurement of the freezing point of its solution in benzene, that this liquid is a polymeride of keten, formed according to the equation $2CH_2{:}CO = C_4H_4O_2$. We also showed that the substance undergoes a series of reactions which indicate a close relation with acetoacetic acid. Thus, with water in the cold, acetoacetic acid itself is produced:

$$C_4H_4O_2 + H_2O = CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2H;$$

on boiling with alkalis, acetates are formed:

$$C_4H_4O_2 + Ba(OH)_2 = Ba(C_2H_3O_2)_2;$$

with aniline, a very vigorous reaction takes place, resulting in the formation of acetoacetanilide:

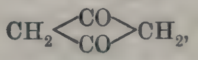
$$C_4H_4O_2 + C_6H_5{\cdot}NH_2 = CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_5;$$

and with phenylhydrazine, a phenylhydrazone-phenylhydrazide of acetoacetic acid is obtained:

$$C_4H_4O_2 + 2C_6H_5{\cdot}N_2H_3 = CH_3{\cdot}C({:}N{\cdot}NHPh){\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NHPh + H_2O.$$

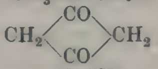
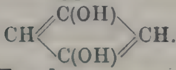
The hydrazide character of the latter substance was shown by the formation of a hydrochloride and of a platinichloride. Addition of pyridine to the polymeride caused a violent reaction, with the formation of brown resins; but when the reaction was allowed to take place in benzene solution, dehydracetic acid was the chief product.

All these facts led us to conclude that the polymeride still contained a keten group, and we therefore assumed it to be acetylketen, having the formula $\mathrm{CH_3{\cdot}CO{\cdot}CH{:}CO}$. At the same time, we considered the possibility of its being *cyclo*butan-1 : 3-dione :



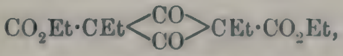
$$\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{CO}}>\mathrm{CH_2},$$

as this would agree better with our observation that it did not appear to react with alcohol. Nevertheless, the great reactivity and very unsaturated nature of the substance led us to prefer the keten formula, and a measurement of the refractive index also seemed to support this choice :

	M.R.
$\mathrm{CH_3{\cdot}CO{\cdot}CH{:}CO}$	20·489
 $\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{CO}}>\mathrm{CH_2}$	18·782
 $\mathrm{CH}\lessgtr\genfrac{}{}{0pt}{}{\mathrm{C(OH)}}{\mathrm{C(OH)}}\gtrless\mathrm{CH}$	20·664
Found	20·075

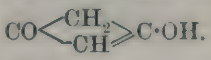
Here, however, we had to suppose that the $\mathrm{{\cdot}CH{:}CO}$ group had a depressing action on the refractive index, an assumption which, on account of lack of experimental evidence, we made with all reserve.

After the publication of the previous paper, the work was for a time interrupted, and it was not until the session just closed that it could be seriously resumed. In the meantime a paper by Staudinger and Bereza has appeared (*Ber.*, 1909, **42**, 4908), in which the polymerisation of the disubstituted keten, ethyl ethylketencarboxylate, $\mathrm{CO{:}CEt{\cdot}CO_2Et}$, is described, the product according to these authors being undoubtedly a *cyclo*butane derivative, namely, ethyl 1 : 3-diethyl*cyclo*butan-2 : 4-dione-1 : 3-dicarboxylate,



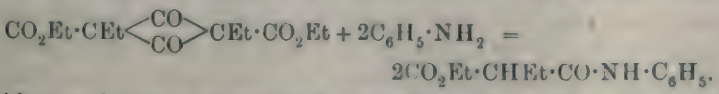
$$\mathrm{CO_2Et{\cdot}CEt}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{CO}}>\mathrm{CEt{\cdot}CO_2Et},$$

and on this and other grounds they conclude that the substance discovered by us must be Δ^1-*cyclo*buten-1-ol-3-one,



$$\mathrm{CO}<\genfrac{}{}{0pt}{}{\mathrm{CH_2}}{\mathrm{CH}}\geqslant\mathrm{C{\cdot}OH}.$$

The arguments of Staudinger and Bereza did not, however, seem to us to be necessarily convincing. Thus, ethyl 1 : 3-diethyl*cyclo*butan-2 : 4-dione-1 : 3-dicarboxylate reacts with two molecular proportions of aniline to form two molecules of ethyl ethylmalonanilate :



$$\mathrm{CO_2Et{\cdot}CEt}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{CO}}>\mathrm{CEt{\cdot}CO_2Et} + 2\mathrm{C_6H_5{\cdot}NH_2} = 2\mathrm{CO_2Et{\cdot}CHEt{\cdot}CO{\cdot}NH{\cdot}C_6H_5}.$$

Also, on heating, the diethyl ester dissociates with regeneration of ethyl ethylketencarboxylate. Our substance, on the other hand, reacts with only one molecular proportion of aniline, and it shows no tendency to dissociate on heating—quite the contrary. Similar remarks apply also to the reactions of truxilic acid referred to by Staudinger and Bereza in this connexion. Again, the comparative stability of the polymeride of keten, both in the pure state and in alcoholic solution, which Staudinger and Bereza cite as being inconsistent with the keten formula, was not conclusive, more especially as our previous observations on these points were incomplete. We have since found that alcohol reacts with the polymeride if a trace of mineral acid be present, forming acetoacetic ester:

$$C_4H_4O_2 + C_2H_5\cdot OH = CH_3\cdot CO\cdot CH_2\cdot CO_2\cdot C_2H_5\,;$$

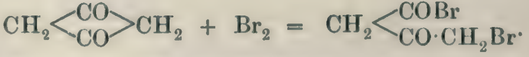
and that, when the pure substance is kept for some weeks in sealed tubes at the ordinary temperature, dehydracetic acid is formed, apparently by direct polymerisation. Moreover, Staudinger and Bereza show that disubstituted ketens become much less reactive when one of the substituents is an acidic group, and, consequently, it was not unreasonable to assume, as we did, that the substitution of acetyl for a hydrogen atom in keten should have a similar effect.

So far therefore there was not sufficient evidence available to allow of a definite conclusion being drawn between the open chain and the cyclic formula for the first polymeride of keten. Most of the reactions described above involved a transference of a hydrogen atom from the reagent to the polymeride, and there was nothing to show into which part of the molecule of the latter this atom had entered.

It occurred to us that a study of the action of bromine on the polymeride might throw some light on its constitution. We found that bromine combined directly with the substance, forming a monobromoacetoacetyl bromide, which, on treatment with alcohol, gave the corresponding ethyl monobromoacetoacetate. If the polymeride had the acetylketen structure, addition of bromine should give the α-bromoacetoacetyl bromide:

$$CH_3\cdot CO\cdot CH{:}CO + Br_2 = CH_3\cdot CO\cdot CHBr\cdot COBr,$$

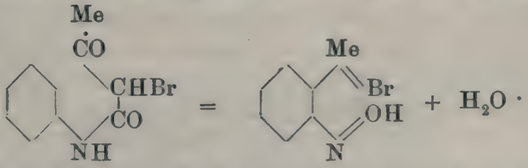
whereas from *cyclo*butan-1:3-dione only the γ-derivative could result:



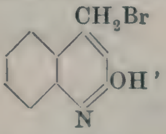
$$CH_2{<}\begin{matrix}CO\\CO\end{matrix}{>}CH_2 \;+\; Br_2 \;=\; CH_2{<}\begin{matrix}COBr\\CO\cdot CH_2Br\end{matrix}.$$

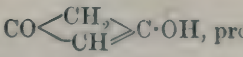
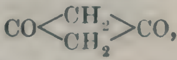
Since we have actually obtained the γ- and not the α-derivative under conditions which rendered a wandering of the bromine atom from the α- to the γ-position highly improbable, it follows that the evidence in favour of the cyclic structure for the first polymeride of keten is now conclusive. It may be noted, however, in passing, that the substance may still be regarded as an internal anhydride of acetoacetic acid. The true acetylketen has therefore yet to be discovered, but we venture to prophesy that, when prepared, it will resemble *cyclo*butan-1 : 3-dione in many of its reactions.

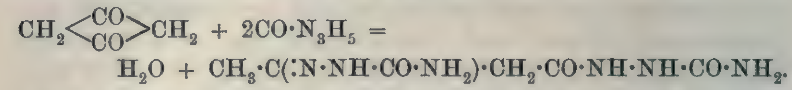
Incidentally, by treating the above-mentioned γ-bromoacetoacetyl bromide with aniline, we have obtained the same bromoacetoacetanilide as was prepared by Knorr (*Annalen*, 1886, **236**, 79) by the bromination of acetoacetanilide, and, by digesting this with concentrated sulphuric acid as described by him, we also obtained his bromo-2-hydroxy-4-methylquinoline (*loc. cit.*, p. 91). Knorr also prepared a substance, which he believed to be identical with the latter compound, by the action of bromine water on 2-hydroxy-4-methylquinoline itself. As under these conditions the bromine would almost certainly occupy the 3-position, Knorr assumed that his bromoacetoacetanilide was the α-derivative, the condensation with sulphuric acid taking place according to the equation:



We now find, however, that the compound formed on brominating 2-hydroxy-4-methylquinoline is not identical with, but is an isomeride of, the bromo-2-hydroxy-4-methylquinoline produced by the action of sulphuric acid on bromoacetoacetanilide; and, since our synthesis shows that the latter substance undoubtedly has the bromine in the γ-position, it follows that the compound obtained from it by the action of sulphuric acid is ω-bromo-2-hydroxy-4-methylquinoline:

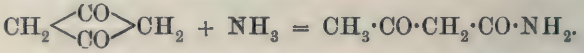


The semi-enolic formula,  $CO{<}^{CH_2}_{CH}{\geqslant}C{\cdot}OH$, proposed by Staudinger and Bereza agrees better than the diketonic formula,  $CO{<}^{CH_2}_{CH_2}{>}CO$, with the molecular volume, refractive index, and dispersion of the substance, as we shall show later; but we can find no chemical evidence for it. *cyclo*Butan-1 : 3-dione does not appear to react with sodium, with acetyl chloride, or with phenylcarbimide. In fact, a mixture of it with phenylcarbimide may be separated into its constituents by fractional distillation. It may be mentioned, however, in this connexion that the substance gives a red colour with ferric chloride in alcoholic solution. The semi-enolic formula is also inconsistent with the reaction with phenylhydrazine, this substance reacting normally with β-diketones, which can exist in the semi-enolic form to form a pyrazole ring. The reaction with phenylhydrazine is supported by that with semicarbazide, two molecular proportions of which react with *cyclo*butan-1 : 3-dione to form a semicarbazone-semicarbazide of acetoacetic acid:



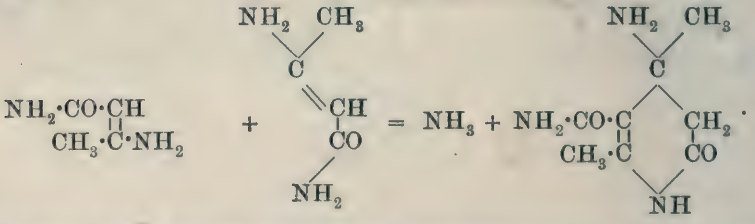
$$CH_2{<}\substack{CO\\CO}{>}CH_2 + 2CO{\cdot}N_3H_5 = H_2O + CH_3{\cdot}C({:}N{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2.$$

Dry ammonia combines with *cyclo*butan-1 : 3-dione at low temperatures to form acetoacetamide, previously prepared by Claisen and Meyer (*Ber.*, 1902, **35**, 583) by the prolonged action of dilute aqueous ammonia on acetoacetic ester:

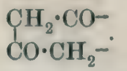


$$CH_2{<}\substack{CO\\CO}{>}CH_2 + NH_3 = CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NH_2.$$

By the further action of dry ammonia, acetoacetamide is converted into a yellow oil. This oil could not be purified, but it appeared to consist mainly of the hitherto non-isolated amide of β-aminocrotonic acid, $CH_3{\cdot}C(NH_2){:}CH{\cdot}CO{\cdot}NH_2$, for, on heating it in a current of dry hydrogen, a crystalline substance was produced, melting at 197°, and having the empirical formula $C_8H_{13}O_2N_3$. From analogy to the condensation of acetoacetamide described by Claisen and Meyer, this crystalline substance is probably 4-*amino*-2 : 4-*dimethyl*-Δ^2-*tetrahydro*-6-*pyridone*-3-*carboxylamide*, formed thus:



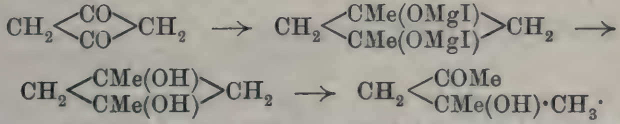
From its reactions the stability of the *cyclo*butan-1 : 3-dione ring is thus seen to be very small, even when compared with that of *cyclo*butane prepared by Willstätter and Bruce (*Ber.*, 1907, **40**, 3979). In fact, the substance behaves as if the ring were not completely closed, that is to say, as if its constitution were:



$$\begin{array}{l} CH_2{\cdot}CO{-} \\ CO{\cdot}CH_2{-} \end{array}.$$

Since, however, there is no precedent for such a formula as this, we are not prepared seriously to propose it.

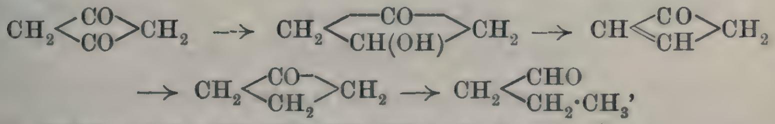
The action of Grignard's reagent (in this case magnesium methyl iodide) gave for the most part only by-products which could not be identified, but there was some indication of the formation of diacetone alcohol, which was probably produced somewhat as follows:



$$\mathrm{CH_2}{<}\substack{\mathrm{CO}\\ \mathrm{CO}}{>}\mathrm{CH_2} \longrightarrow \mathrm{CH_2}{<}\substack{\mathrm{CMe(OMgI)}\\ \mathrm{CMe(OMgI)}}{>}\mathrm{CH_2} \longrightarrow$$

$$\mathrm{CH_2}{<}\substack{\mathrm{CMe(OH)}\\ \mathrm{CMe(OH)}}{>}\mathrm{CH_2} \longrightarrow \mathrm{CH_2}{<}\substack{\mathrm{COMe}\\ \mathrm{CMe(OH)\cdot CH_3}}.$$

Reduction of *cyclo*butan-1 : 3-dione with hydrogen in the presence of platinum black gave an unlooked-for result, *n*-butyraldehyde being formed. The reaction may possibly take place in the following stages:



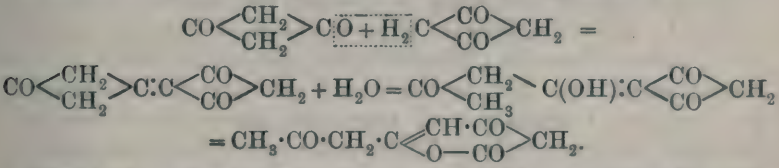
$$\mathrm{CH_2}{<}\substack{\mathrm{CO}\\ \mathrm{CO}}{>}\mathrm{CH_2} \longrightarrow \mathrm{CH_2}{<}\substack{\text{—CO—}\\ \mathrm{CH(OH)}}{>}\mathrm{CH_2} \longrightarrow \mathrm{CH}{\ll}\substack{\mathrm{CO}\\ \mathrm{CH}}{>}\mathrm{CH_2}$$

$$\longrightarrow \mathrm{CH_2}{<}\substack{\text{CO—}\\ \mathrm{CH_2}}{>}\mathrm{CH_2} \longrightarrow \mathrm{CH_2}{<}\substack{\mathrm{CHO}\\ \mathrm{CH_2\cdot CH_3}},$$

or $\mathrm{C_4H_4O_2 + 6H = CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO + H_2O}$.

As the intermediate compounds have not been isolated, it is not possible to say exactly at what stage the ring is broken. The elimination of water would be facilitated by the dehydrating action of unchanged *cyclo*butan-1 : 3-dione.

The further polymerisation of *cyclo*butan-1 : 3-dione to dehydracetic acid may perhaps be represented by the following scheme, although many others are possible, especially if *cyclo*butan-1 : 3-dione be given the open-chain structure suggested above:



$$\mathrm{CO}{<}\substack{\mathrm{CH_2}\\ \mathrm{CH_2}}{>}\mathrm{C}\boxed{\mathrm{O+H_2}}\mathrm{C}{<}\substack{\mathrm{CO}\\ \mathrm{CO}}{>}\mathrm{CH_2} =$$

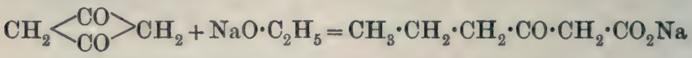
$$\mathrm{CO}{<}\substack{\mathrm{CH_2}\\ \mathrm{CH_2}}{>}\mathrm{C{:}C}{<}\substack{\mathrm{CO}\\ \mathrm{CO}}{>}\mathrm{CH_2} + \mathrm{H_2O} = \mathrm{CO}{<}\substack{\mathrm{CH_2}\\ \mathrm{CH_3}}\diagdown\mathrm{C(OH){:}C}{<}\substack{\mathrm{CO}\\ \mathrm{CO}}{>}\mathrm{CH_2}$$

$$= \mathrm{CH_3{\cdot}CO{\cdot}CH_2{\cdot}C}{\ll}\substack{\mathrm{CH{\cdot}CO}\\ \mathrm{O{-}CO}}{>}\mathrm{CH_2}.$$

Collie's formula for dehydracetic acid (Trans., 1891, **59**, 179) has here been chosen. The condensation would be much more difficult to follow if dehydracetic acid had the formula assigned to it by Feist (*Annalen*, 1890, **257**, 253).

Much work has been done with a view to discovering the constitution of the yellow substance which is formed from *cyclo*butan-1 : 3-dione in the presence of quinoline; but, on account of the small quantity available, not much success has been obtained.

In our former paper we stated that "acetylketen" combined with sodium ethoxide in dry alcohol to form sodium ethylacetoacetate, which, on boiling with hydrochloric acid, gave carbon dioxide and methyl propyl ketone. Since the polymeride of keten is in reality *cyclo*butan-1 : 3-dione, the compound formed with sodium ethoxide must have been sodium butyrylacetate, which, however, would also give methyl propyl ketone on boiling with hydrochloric acid:



$$CH_2\left<\begin{matrix}CO\\CO\end{matrix}\right>CH_2 + NaO{\cdot}C_2H_5 = CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2Na$$

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2Na + HCl = NaCl + CO_2 + CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3.$$

We propose to study this type of reaction more fully.

*cyclo*Butan-1:3-dione does not react with hydrocyanic acid, even when the two substances are heated on the water-bath in sealed tubes, and it does not react with liquid cyanogen at the ordinary temperature.

EXPERIMENTAL.

Preparation of cyclo*Butan*-1:3-*dione.*

We have not succeeded greatly in improving the yield of *cyclo*butan-1:3-dione, about 5 grams from 150 grams of acetic anhydride being the best hitherto obtainable. It is not necessary to fractionate the crude keten, beyond allowing the temperature to rise to about −80° to −70°, before distilling it into the pressure tubes. There seems to be little risk of explosion if the tubes are carefully made, and they may be handled with safety after polymerisation has taken place, as the internal pressure will then have diminished. They should, however, be re-cooled to about −80° before being opened, or loss of substance may be caused by the rush of gas. Diluting the keten with ether to diminish the violence of the polymerisation did not noticeably improve the yield; but, on the other hand, surrounding the tube containing the keten with a bath of alcohol cooled to −30°, or lower, and allowing the whole slowly to attain the temperature of the room, materially reduced the formation of brown resins. To ensure complete polymerisation, the tubes should be kept for a day or two before being opened. The distillation of the *cyclo*butan-1:3-dione is conveniently carried out under about 30 mm. pressure, when the bulk of the substance passes over as the temperature of the bath rises from 40° to 60°. The temperature should, however, finally be raised to about 100°. The liquid then remaining in the distilling flask consists of dehydracetic acid and brown resins. The distilling flask should be heated by a water- or oil-bath, and not by a naked flame, or the distillate may be contaminated with decomposition products from the residue. The whole apparatus should, of course, be carefully dried and filled with dried air before commencing the distillation; and only dried air should be allowed to enter the apparatus during and at the close of the operation. These precautions are especially necessary when it is intended to study the physical properties of the substance. The preparation of *cyclo*butan-1 : 3-dione may be recommended as a useful exercise for students in laboratories where a supply of liquid air is available.

Physical Properties of cyclo*Butan*-1 : 3-*dione.*

We have confirmed the boiling point of *cyclo*butan-1 : 3-dione under 760 mm. pressure previously given. Under 100 mm. pressure the substance boils at 69—71° (corr.). The freezing point of a carefully prepared sample was found to be $-7{\cdot}9^\circ$ to $-7{\cdot}5^\circ$.

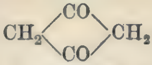
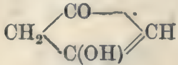
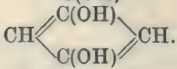
The density of two samples of the substance was determined at various temperatures. As a mean of four weighings (0·7432, 0·7433, 0·7432, 0·7433), the pyknometer contained 0·74325 gram of water weighed in air at 18°. The weights of *cyclo*butan-1 : 3-dione and the densities calculated from these were as follows:

t.	Weight of substance in air.		${}_4\delta_t$.	
	I.	II.	I.	II.
9·5°		0·8238		1·1069
10·5	0·8226		1·1053	
14·1		0·8196		1·1012
14·3	0·8193		1·1008	
17 7	0·8165		1·0969	
18·7		0·8157		1·0958
21·6	0·8130		1·0921	
22·7		0·8123		1·0912
25·3	0·8098		1·0877	
26·7		0·8088		1·0864
29·3	0·8064		1·0830	

The temperatures were measured by means of a thermometer which had been carefully compared with a standard thermometer from the International Bureau of Weights and Measures, and they have been corrected to the hydrogen scale. The densities in each series lie very nearly on a straight line, but there is a difference of from 2 to 4 parts in 10,000 between the two series. The density at 23°, given in our previous paper, is in line with those in the first series. Taking the mean of the two series by graphic interpolation, the density of *cyclo*butan-1 : 3-dione between 10° and 30° is given by the equation:

$${}_4\delta_t = 1{\cdot}1000 - 0{\cdot}00118(t - 15^\circ).$$

Taking the molecular weight as 84·03, the molecular volume at 15° is 76·39. Assuming Traube's values for the atomic volumes at 15° (Traube, *Grundriss der physikalischen Chemie*, 1904, p. 120; Smiles, *Chemical Constitution and Physical Properties*, 1910. p. 125): $C = 9{\cdot}9$; $H = 3{\cdot}1$; $O_{CO} = 5{\cdot}5$; $O_{OH} = 2{\cdot}3$; ring formation = $-8{\cdot}1$, and molecular co-volume = 25·9, we obtain the following calculated values:

	M.V.$_{15^\circ}$
	80·8
	77·5
	74·4
$CH_3 \cdot CO \cdot CH{:}CO$	88·9
Found	76·4

This property is therefore decisively in favour of a cyclic formula. The enolic formulæ appear to agree better than the diketonic formula, but it is quite possible that the contraction due to the formation of the *cyclo*butane ring is more than 8·1 units, this number having been obtained mainly from a study of benzenoid substances.

The refractive index of *cyclo*butan-1 : 3-dione has been redetermined, using portions of the two samples just mentioned, with the result that the value for the *D* line given in our former paper would seem to have been too low. This may have been due to the precautions to exclude moisture having been insufficient. The densities were interpolated from the values given above:

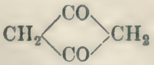
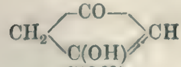
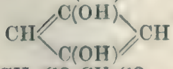
First Sample.

Line.	*t.*	*N.*	$_4\delta_t$.	M.R.
C	18·7°	1·43490	1·0957	20·007
D_1	19·2	1·43769	1·0951	20·131
G'	18·7	1·45179	1·0957	20·680

Second Sample.

Line.	*t.*	*N.*	$_4\delta_t$.	M.R.
C	18·6°	1·43547	1·0958	20·029
D_1	18·3	1·43877	1·0961	20·157
G'	18·7	1·45236	1·0957	20·702

Both sets of numbers give as the value for the molecular "dispersion," 0·673. For comparison, the values for the molecular refractivities and dispersion, calculated from the atomic refractivities given in Landolt and Börnstein's "*Tabellen*" for the various isomeric formulæ, will be found in the table herewith:

	C.	D_1	$G' - C$.
	18·53	18·78	0·47
	19·54	19·72	0·64
	20·56	20·66	0·80
$CH_3 \cdot CO \cdot CH{:}CO$	20·36	20·49	0·70
Found	20·02	20·14	0·67

From these figures it would appear that of the possible ring formulæ the semi-enolic modification is the most probable. The very unsaturated nature of the substance, however, makes it legitimate to assume the existence of an exaltation of the refractive index and dispersion which would raise the values calculated for the diketonic formula by an amount rather less than that due to a double bond.

The study of the absorption spectrum has been kindly repeated for us by Professor E. C. C. Baly, using various thicknesses of a 0·1 molar solution in dry ether. The result was to confirm the observation of Mr. H. E. Watson given in our former paper. There was no selective absorption, and only a slight general absorption in the ultra-violet.

Analysis of cyclo*Butan*-1 : 3-*dione*.—As a further check on the composition, a third analysis of the substance was made:

0·1298 gave 0·2704 CO_2 and 0·0599 H_2O. C = 56·8; H = 5·1.

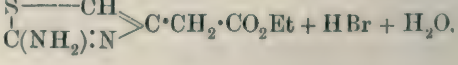
$C_4H_4O_2$ requires C = 57·1; H = 4·8 per cent.

Action of Alcohol on cyclo*Butan*-1 : 3-*dione*.—As stated earlier in the paper, *cyclo*butan-1 : 3-dione combines with ethyl alcohol in the presence of a trace of mineral acid. To about 0·5 gram of the compound dissolved in ethyl alcohol, a small quantity of a dilute alcoholic solution of sulphuric acid (ethylsulphuric acid) was added. After two days the odour of *cyclo*butan-1 : 3-dione had disappeared. The free acid was neutralised by shaking with moist calcium carbonate, and the mixture was dried with calcium chloride, filtered, and distilled—towards the end under diminished pressure. The last fraction had the odour of acetoacetic ester, gave the characteristic violet colour with aqueous ferric chloride, and boiled at 182°/760 mm. (corr.), pure acetoacetic ester boiling at 181°.

Action of Bromine on cyclo*Butan*-1 : 3-*dione*: γ-*Bromoacetoacetyl Bromide*.

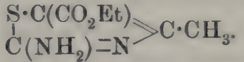
In order to study the action of bromine on *cyclo*butan-1 : 3-dione, these substances were diluted with carbon tetrachloride, which had been dried over calcium chloride and distilled. The bromine was purified by washing with aqueous potassium bromide and then with water, and distilling from phosphoric oxide. In a preliminary experiment a dilute solution of *cyclo*butan-1 : 3-dione was titrated with a bromine solution, using the colour of the bromine as indicator. The strength of the bromine solution was found in the usual way by shaking with aqueous potassium iodide and titrating with thiosulphate. The titration of the *cyclo*butan-1 : 3-dione was not very sharp, as towards the end the reaction became very slow, but it was sufficient to show that the substances reacted in molecular proportions. 0·384 Gram of *cyclo*butan-1 : 3-dione required 0·707 gram of bromine, whilst according to the equation $C_4H_4O_2 + Br_2 = C_4H_4O_2Br_2$, 0·732 gram should have been used. To carry out the bromination on a larger scale, *cyclo*butan-1 : 3-dione, in weighed quantities of from 2 to 5 grams, was dissolved in about 50 c.c. of carbon tetrachloride contained in a 100 c.c. measuring flask. An equivalent amount of bromine, dissolved in 20 to 30 c.c. of carbon tetrachloride, was then run in very slowly from a burette, the flask meanwhile being kept immersed in cold water and well shaken. The reaction appeared to be over when a little more than 95 per cent. of the bromine had been added. The solution of the acid bromide fumed strongly on contact with moist air, and reacted vigorously with water, giving hydrobromic acid. To prepare the ester, alcohol, which had been dehydrated by means of metallic calcium, was added to the solution of the acid bromide. The substances reacted at once with evolution of heat, and the hydrogen bromide which was formed, being much less soluble in carbon tetrachloride than in the ester, "salted out" the latter, which formed a light brown layer on top of the tetrachloride. We have found that the same thing occurs if carbon disulphide is used as solvent in place of the tetrachloride. This phenomenon must have been observed in brominating ethyl acetoacetate in the ordinary way, but we have not seen it mentioned. On shaking the mixture with water, the ester at once dissolved in the carbon tetrachloride. The washing with water was continued until all free acid had been removed. The solution was then dried over calcium chloride, the carbon tetrachloride and any alcohol remaining were evaporated, and the residue was distilled under 10 mm. pressure, the bulk of the ester passing over between 110° and 115°. This is about 15° lower than the boiling point of the γ-bromoacetoacetic ester under 10 mm. pressure given by Epprecht (*Annalen*, 1894, **278**, 77); but, as this author does not state that the mercury in his manometer had been properly boiled out, the pressure in his apparatus was probably rather higher. The presence of bromine in the ester was proved by warming with dilute sodium hydroxide, sodium bromide being formed. With copper sulphate and sodium acetate, a bright green copper salt was produced. The γ-position of the bromine in the ester was also shown by the reaction with thiocarbamide, as described by Epprecht (*loc. cit.*), ethyl 2-aminothiazolyl-4-acetate, melting at 93—94°, being obtained according to the equation:

$CH_2Br\cdot CO\cdot CH_2\cdot CO_2Et + CS(NH_2)_2 =$



$$\begin{array}{l} S\text{———}CH \\ | \\ C(NH_2){:}N \end{array}\!\!>C\cdot CH_2\cdot CO_2Et + HBr + H_2O.$$

Ethyl α-bromoacetoacetate would have given with thiocarbamide, ethyl 2-amino-4-methylthiazole-5-carboxylate, melting at 175°:



$$\begin{matrix} S\cdot C(CO_2Et) \\ | \\ C(NH_2){=}N \end{matrix} \!\!>\! C\cdot CH_3.$$

It is well known, however, that in certain circumstances the α-bromo-ester may be converted into the γ-bromo-ester by the action of hydrogen bromide, and it occurred to us that this might possibly have taken place when the alcohol was added to the acid bromide. The "salting out" of the ester by the hydrogen bromide would certainly facilitate such an interchange. Accordingly, the synthesis of the ester was repeated in a slightly different way. The solution of the acid bromide was run very slowly into excess of alcohol, in which finely ground, dry sodium acetate was suspended, the mixture being kept well stirred during the process. The bromination of the *cyclo*butan-1 : 3-dione and the reaction with alcohol were both carried out at 0°. This time no "salting out" of the ester took place. The solution was washed with water, dried, and concentrated as before, but the ester was distilled under 5 mm. pressure, and passed over below 100°, leaving only a very small residue in the distilling flask. The yield of ester was about 75 per cent. of that calculated from the weight of *cyclo*butan-1 : 3-dione taken. The ester thus obtained was quite colourless. The thiazole derivative was also very nearly colourless, but it melted as before at 93° (corr.), even after repeated recrystallisation from ether.

To prepare γ-bromoacetoacetanilide, a little less than one molecular proportion of aniline dissolved in carbon tetrachloride was added slowly to a solution of γ-bromoacetoacetyl bromide in the same solvent. The anilide separated at once in the form of an almost white precipitate, which, after washing with water and drying, melted at about 134°. On recrystallising from alcohol, colourless crystals were obtained, which melted and decomposed at 138° (corr.), as given by Knorr (*Annalen*, 1886, **236**, 79) for the bromoacetoacetanilide which he obtained by brominating acetoacetanilide. The identification was confirmed by taking a mixed melting point with a sample of bromoacetoacetanilide prepared by Knorr's method. When more than one molecular proportion of aniline was added to the acid bromide, the second bromine atom was also attacked, and tarry substances were formed, from which a pure product could not be isolated. On dissolving the bromoacetoacetanilide in cold concentrated sulphuric acid, keeping the solution overnight, and then pouring into water, bromo-2-hydroxy-4-methylquinoline was precipitated, which, after recrystallising from alcohol and drying, formed the curious felt-like mass described by Knorr, which melted and decomposed at 260° (corr.). Knorr (*loc. cit.*,

p. 92) gives the melting point as "circa 258°." For comparison, a sample of bromo-2-hydroxy-4-methylquinoline was prepared by the other method described by Knorr (*loc. cit.*, p. 91). 2-Hydroxy-4-methylquinoline, obtained by digesting acetoacetanilide in the cold with concentrated sulphuric acid, was suspended in warm water, and to the mixture bromine water was added until a permanent yellow colour was produced, slightly more than one molecular proportion of bromine being required. The resulting bromo-2-hydroxy-4-methylquinoline was washed with water and recrystallised repeatedly from alcohol. In appearance it was indistinguishable, even under the microscope, from the bromohydroxymethylquinoline prepared from bromoacetoacetanilide, but it melted, apparently without decomposing, at 273—275° (corr.), although it began to soften at 269—270°. A mixture of the two preparations melted at 240°.

The γ-bromoacetoacetyl bromide was evidently an unstable substance, as its solutions began to turn brown after a few hours. Nevertheless an attempt was made to isolate it in a pure state. A solution of it in carbon tetrachloride was prepared as before, starting with about 5 grams of *cyclo*butan-1:3-dione. The carbon tetrachloride was removed by distilling under diminished pressure (100 to 30 mm.), and the liquid remaining in the flask was distilled under 5 mm. pressure in a current of dry hydrogen. Between 1 and 2 grams of an oily liquid passed over between 105° and 110°, but hydrogen bromide was evolved at the same time, and a large amount of a dark-coloured residue remained in the flask. The liquid appeared colourless while on the end of the condenser tube, but was light brown when observed in the test-tubes placed to collect it. The best sample was sealed up as quickly as possible. It gradually darkened on keeping, and after a few days was nearly opaque. The other samples reacted vigorously with water, with alcohol, and with aniline, and fumed strongly in moist air. The residue in the distilling flask appeared to consist largely of free carbon. A small proportion, however, was soluble in chloroform, and the solution, when placed on the skin and washed with water, gave rise to a brilliant violet stain, which was very stable.

Action of Semicarbazide on cyclo*Butan-1:3-dione.*

To prepare the semicarbazide derivative, *cyclo*butan-1:3-dione was treated with an aqueous solution of semicarbazide hydrochloride containing an excess of sodium acetate. A crystalline precipitate was formed on keeping, which separated from warm water in small, rhombic (?) crystals, melting and decomposing slightly at 217—218°. The substance was insoluble in non-aqueous solvents, but was very soluble in dilute hydrochloric acid, and from this solution platinic chloride precipitated a sparingly soluble platinichloride. Owing to the small solubility of the base in cold water, and to the fact that it was decomposed by boiling water, the molecular weight could not be determined. Analysis, however, showed that it was the *semicarbazone-semicarbazide* of *acetoacetic acid*:

0·1210 gave 0·1448 CO_2 and 0·0626 H_2O. $C=32·6$; $H=5·6$.
0·1135 „ 0·1388 CO_2 „ 0·0570 H_2O. $C=33·4$; $H=5·6$.
0·1106 „ 37·1 c.c. N_2 (dry) at 17° and 751 mm. $N=39·0$.
$C_6H_{12}O_3N_6$ requires $C=33·3$; $H=5·6$; $N=38·9$ per cent.

Action of Ammonia on cyclo*Butan*-1 : 3-*dione*.

To follow the reaction with ammonia, *cyclo*butan-1 : 3-dione in quantities of about 3 grams was dissolved in dry ether and placed in a U-tube, which was immersed in a freezing mixture of ice and salt, kept at −10° to −15°. A slow current of ammonia gas, produced by warming aqueous ammonia, and dried by passing first through a 50 per cent. solution of potassium hydroxide and then over freshly ignited lime, was then passed through the solution in the U-tube. Almost immediately a solid substance commenced to separate out; but after about twenty minutes oily drops of a yellow colour began to make their appearance. The reaction was then stopped, and the solid substance was quickly scraped on to a porous plate, which had previously been cooled to 0°. If the temperature was allowed to rise, or if the action of the ammonia was prolonged, the solid was completely converted into the yellow oil, from which it could not again be recovered. The solid substance, after drying on the porous plate, was usually pure (m. p. 54°, corr.). It was insoluble in ether, but very soluble in water, alcohol, or glacial acetic acid. It could, however, be recrystallised most conveniently from a mixture of acetone and light petroleum. The crystals were colourless. The aqueous solution gave the violet colour characteristic of acetoacetic ester. On warming with aqueous alkalis, ammonia was evolved, and if this solution was boiled with hydrochloric acid, carbon dioxide and acetone were given off, the latter being identified by the iodoform reaction, the alkaline mercuric chloride test, and the formation with benzaldehyde of distyryl ketone, melting at 112° (corr.). Heating the substance directly with hydrochloric acid caused decomposition with formation of brown compounds. On adding ammoniacal copper sulphate to the aqueous solution of the substance and neutralising the ammonia, a green *copper* salt was formed:

0·1071 gave 0·1871 CO_2 and 0·0667 H_2O. C=47·6; H=6·9.
0·0765, in 19·59 glacial acetic acid, gave $\Delta t = -0·157°$. M.W.=97.
0·0798, „ 19·59 „ „ „ „ $\Delta t = -0·158°$. M.W.=101.
$C_4H_7O_2N$ requires C=47·5; H=6·9 per cent. M.W.=101.

The substance is therefore identical with the acetoacetamide described by Claisen and Meyer (*Ber.*, 1902, **35**, 583), for which, however, they give a melting point of 50°. They did not determine the molecular weight.

The yellow oil formed by the further action of ammonia on acetoacetamide appears to bear some resemblance to the substance obtained by Duisberg (*Annalen*, 1882, **213**, 174) by the action of ammonia on acetoacetic ester, from which, however, this author was unable to isolate a compound having a definite composition. It is best prepared by the prolonged action of ammonia on *cyclo*butan-1:3-dione at −10° to −15°. If the reaction is started at the ordinary temperature, much heat is evolved, and coloured decomposition products are formed. The **U**-tube may, however, be removed from the freezing mixture as soon as all the solid acetoacetamide has disappeared. The oil thus obtained always contained excess of ammonia, which could not be completely removed, even by passing a current of dry hydrogen through it for many hours, or by leaving it over sulphuric acid in a vacuum desiccator for several months, although the pressure was sometimes reduced to 2 to 3 mm. As it was not soluble in any solvents which did not mix with water, it could not be purified by washing. It was readily soluble in water or alcohol, less readily so in acetone, and insoluble in ether, benzene, light petroleum, chloroform, or carbon tetrachloride. On exposure to moist air, a crystalline substance was formed, which, after drying on a porous plate, melted at 147°. A quantity of this sufficient for an analysis could not, however, be obtained. On passing a current of dry hydrogen through the yellow oil at 110°, ammonia and water were given off. At the end of an hour the substance had become very viscous, and a portion taken out on a glass rod solidified on cooling. The remainder was then washed out of the tube with warm acetone, and, on cooling the solution, a colourless, crystalline compound separated out, which melted at 197° (corr.). Recrystallisation from acetone did not alter the melting point. The compound was readily soluble in water, alcohol, or glacial acetic acid, sparingly so in cold acetone, and insoluble in ether, benzene, or light petroleum. On warming with aqueous alkalis, ammonia was evolved. For a quantitative estimation of the ammonia, the substance was distilled with 2*N*-potassium hydroxide solution, the ammonia being caught in standard acid:

0·1133 gave 0·2176 CO_2 and 0·0743 H_2O. C=52·4; H=7·3.
0·1063 „ 21·5 c.c. N_2 (moist) at 19° and 752·8 mm. N=22·9.
0·0765, in 17·75 glacial acetic acid, gave $\Delta t = -0·092°$. M.W.=183.
0·0989, „ 17·75 „ „ „ „ $\Delta t = -0·128°$. M.W.=170.

$C_8H_{13}O_2N_3$ requires C=52·5; H=7·1; N=22·9 per cent.
M.W.=183.

0·2369 gave 0·0233 NH_3, that is, 183 grams $C_8H_{13}O_2N_3$ gave 18·0 grams NH_3.

As stated on p. 1982, we consider the substance to be 4-*amino*-2 : 4-*dimethyl*-Δ^2-*tetrahydro*-6-*pyridone*-3-*carboxylamide*, 183 grams of which should give 17 grams of ammonia on distilling with dilute alkalis. On acidifying the alkaline solution from which the ammonia had been distilled with nitric acid, the free 4-amino-2 : 4-dimethyl-Δ^2-tetrahydro-6-pyridone-3-carboxylic acid was not precipitated, but the *silver* and *barium* salts appeared to be insoluble in water. We propose to prepare larger quantities of the amide from acetoacetamide obtained by Claisen and Meyer's method (*loc. cit.*).

Action of Grignard's Reagent on cyclo*Butan*-1 : 3-*dione.*

To study the action of Grignard's reagent (magnesium methyl iodide), from 3 to 4 grams of *cyclo*butan-1 : 3-dione were dissolved in about 50 c.c. of dry ether contained in a large test-tube, and rather more than two molecular proportions of the reagent, dissolved in about 100 c.c. of ether, were placed in a second tube of about 200 c.c. capacity. The reagent was kept at −78° by means of a bath of solid carbon dioxide and alcohol, and the solution of *cyclo*butan-1 : 3-dione was cooled to about −50°, a lower temperature than this causing the solute to crystallise out. The reagent was kept vigorously stirred by means of a current of air dried over phosphoric oxide, and the solution of *cyclo*butan-1 : 3-dione was run in very slowly in a fine stream by means of a wash-bottle arrangement, dry air under pressure being used to drive the liquid over. Even at the low temperature of −78°, a bright yellow precipitate was at once formed. On allowing the temperature to rise, the precipitate turned brownish-red at about −40°, and became almost black above 0°. In this condition only resinous substances appeared to be formed when the mixture was run into ice-water. It was found preferable to add the ethereal mixture slowly, as soon as it had reached −40° to −30°, to a 2*N*-sulphuric acid solution, containing a slight excess of acid, which was kept partly frozen during the mixing by a freezing mixture. At the end of the reaction, the ethereal solution was separated, and the aqueous solution was shaken with fresh ether, which was added to the first. The ethereal solution was dried over calcium chloride and distilled, the pressure being reduced to 50—60 mm. after the ether had been removed. A small amount of liquid passed over at 80—100°, and a few drops of a bright yellow liquid, having a pleasant aromatic odour, at 180—200°. The last portion of this yellow liquid solidified in the condenser tube on cooling to yellow needles, which, after drying on a porous plate, melted at 145—146°. On adding water to the yellow liquid, more of the yellow solid was precipitated, leaving a nearly colourless solution. This was extracted with ether, the ethereal solution dried with calcium chloride, and evaporated, when a small quantity of a high boiling liquid remained. This gave an orange-coloured solution with concentrated sulphuric acid, and, on pouring this into water, a small quantity of an oil was formed, which had an odour resembling that of mesityl oxide. The fraction of the lower boiling point also had an odour resembling that of mesityl oxide, and it gave a bright red colour with concentrated sulphuric acid. A considerable amount of residue remained in the distilling flask, and resinous substances were also formed on neutralising and evaporating the aqueous solution.

Owing to the poor yield, it was not possible to obtain a liquid having a definite boiling point. It is, however, probable from the foregoing that the reaction proceeds, at any rate to a small extent, in the direction indicated on p. 1983. It is evident that some of the intermediate compounds, possibly including the compound formed when only one :CO group has been attacked, are very unstable, readily condensing to form resinous substances.

Reduction of cyclo*Butan*-1 : 3-*dione*.

This reduction promised to be of interest, but the choice of means was limited. On account of the chemical nature of the substance, the more usual reducing agents were inadmissible, and, owing to the tendency to polymerise on heating, Sabatier and Senderens' method was not promising. Accordingly, the method of reduction by means of hydrogen and platinum black was selected.

The hydrogen was prepared from zinc and dilute sulphuric acid, which were free from arsenic. The gas was passed through a tube packed with copper gauze and kept at a red heat to absorb traces of oxygen, which would otherwise have been reduced to water in contact with the platinum black, and it was dried by means of sulphuric acid contained in a spiral wash-bottle. The platinum black was prepared by Loew's method (*Ber.*, 1890, **23**, 289). It was washed until free from chlorides, and was dried in a vacuum over sulphuric acid. The reduction vessel consisted of a large test-tube fitted with a rubber stopper, through which passed inlet and outlet tubes for the hydrogen and a tap funnel. The inlet tube reached to the bottom of the reduction vessel. About 2 grams of platinum black were placed in the reduction tube, and the air in the latter was replaced by hydrogen. The platinum black was then again dried by warming the tube to about 60°, and alternately exhausting with a Fleuss pump and filling with hydrogen. About 4 grams of *cyclo*butan-1 : 3-dione, dissolved in dry ether, were then introduced through the tap funnel, and a slow current of hydrogen was turned on, the lower end of the reaction vessel being placed in a water-bath to prevent cooling during the evaporation of the ether. After about two hours, most of the ether had been driven off, and a spiral condenser fitted with taps, such as was used for collecting keten, was attached to the outlet tube, and was surrounded by a bath of solid carbon dioxide and alcohol, in order to catch any volatile compounds which might otherwise be carried away by the hydrogen. The water-bath was now warmed to about 65°, and was maintained at that temperature by means of an electric heater. After two days the odour of *cyclo*butan-1 : 3-dione could no longer be detected at the outlet tube of the reduction vessel on detaching the condenser, but a strong odour of butyric acid became noticeable when the connecting tubes were opened to the air. The reduction vessel was then completely immersed in the water-bath, and the temperature was raised to about 95°. After a further twelve hours, all the liquid had passed over into the condenser, which was found to contain a white, crystalline solid. A small quantity of a brown residue remained with the platinum. In order to ascertain whether any compounds had been formed which were gaseous at the ordinary temperature, the condenser was attached to a manometer and to the Fleuss pump and exhausted to about 5 mm. pressure. The tap leading to the pump was then closed, and the temperature was allowed to rise. The solid melted at about −20°, but the pressure did not rise above 50 mm., even when the apparatus had attained the temperature of the room. The condenser was then filled with dry air, after which it had to be set aside for a few days. On again opening the taps, it was noticed that a reduction of pressure had taken place, indicating absorption of oxygen. On transferring the contents of the condenser to a distilling flask and distilling, the major portion passed over at 70—80°, and on reducing the pressure to 20 mm., a further portion passed over at about 80°. The first fraction had an odour resembling that of acetaldehyde, but, on exposure to air, a strong odour of butyric acid was developed. This fraction also gave pronounced aldehyde reactions. The fraction of higher boiling point had a strong odour of butyric acid. It was readily soluble in water, was acid to litmus, and liberated carbon dioxide from sodium carbonate with formation of a very soluble crystallisable salt. It boiled at 163—164°/757 mm. (corr.), and, after solidifying in a freezing mixture, it melted at $-7°$ to $-6°$. The substance was therefore *n*-butyric acid, formed by the oxidation in air of the aldehyde. *n*-Butyraldehyde was accordingly the final product of the reduction of *cyclo*butan-1 : 3-dione by the method employed. The intermediate stages of the reaction are suggested on p. 1983. The water formed would, of course, combine with excess of *cyclo*butan-1 : 3-dione to form acetoacetic acid, which, at the temperature of the experiment, would decompose into carbon dioxide and acetone. It was anticipated, from analogy to the reduction of acetoacetic ester with sodium amalgam, that aldol or $\alpha\gamma$-dihydroxybutane might have been formed, but no trace of these could be detected.

Condensation of cyclo*Butan*-1 : 3-*dione.*

In our former paper we stated that "acetylketen" slowly turned brown on keeping at the ordinary temperature, and that brown resins were formed when it was distilled under the atmospheric pressure. We have since found that when *cyclo*butan-1 : 3-dione is heated in sealed tubes on a water-bath to 80—90°, it is converted chiefly into dehydracetic acid, the reaction being complete after two to three hours. A certain amount of brown resins and of carbon dioxide are, however, formed at the same time. Also, in some samples, which had been sealed up in glass tubes and kept at the ordinary temperature, crystals of dehydracetic acid made their appearance after several weeks; but here again brown resins and carbon dioxide were also produced. The yield of dehydracetic acid was, however, the greater the lower the temperature at which condensation took place. Condensation did not appear to be accelerated by the action of light, for a sample of *cyclo*butan-1 : 3-dione, which had been sealed up in a bulb of "uviol" glass and exposed to bright sunlight, did not turn brown more rapidly than other samples kept in the dark at the same temperature. On the other hand, *cyclo*butan-1 : 3-dione is the more stable the lower the temperature at which it has been distilled. From the formation of brown resins and of carbon dioxide along with the dehydracetic acid, it is evident that the condensation follows more than one course.

On account of the manifold reactions of the multiple keten groups, for the study of which dehydracetic acid has been the chief starting point, notably in the hands of Collie and his pupils (compare Trans., 1907, **91**, 1806), the proof of the formation of this compound from *cyclo*butan-1 : 3-dione, and consequently from keten itself, was of special importance. After recrystallisation, the dehydracetic acid melted at 109° (corr.), and the melting point was not altered by mixing with a sample of pure dehydracetic acid from other sources. Under the microscope the two samples appeared to be identical when they had been crystallised in the same way. The dehydracetic acid from *cyclo*butan-1 : 3-dione also gave an orange colour with ferric chloride. Finally, it was converted by the usual method into diacetylacetone, which was identified by the yellow barium salt and the characteristic violet colour with ferric chloride.

Condensation of cyclo*Butan*-1 : 3-*dione in Presence of Quinoline.*

The condensation of *cyclo*butan-1 : 3-dione in the presence of quinoline has also been further investigated. Quantities of about 5 grams of *cyclo*butan-1 : 3-dione were mixed with an approximately equal amount of pure quinoline in a wide test-tube, to which was fitted a rubber stopper and a mercury valve to allow of the escape of gas and at the same time to exclude air. After two or three days yellow crystals appeared in the tube, and the supernatant liquid became dark brown, while carbon dioxide was slowly given off. After ten days to a fortnight the reaction appeared to be complete, and the contents of the tube, now become very viscous, were scraped out into a mortar and ground up with acetone, in which the yellow crystals were not soluble. The yellow substance was then collected and washed thoroughly with acetone, after which it was dissolved in hot glacial acetic acid and reprecipitated by the addition of water. It was usually pure after one such recrystallisation, melting at 244° (corr.). (In our former paper we gave 231° as the melting point, but the substance then available was not quite pure.) The yield was not good, being only about 20 per cent. of the weight of *cyclo*butan-1 : 3-dione taken, and this was much reduced if impure quinoline had been used. The acetone filtrate from the yellow compound was dark reddish-brown when viewed by transmitted light, and had a marked green fluorescence by reflected light. It contained only resinous substances, from which a pure compound could not be isolated.

It was difficult to obtain satisfactorily consistent analytical numbers, probably owing to the formation of methane on heating:

0·0848 gave 0·2258 CO_2 and 0·0367 H_2O. C = 72·6; H = 4·8.
0·1100 „ 0·2931 CO_2 „ 0·0468 H_2O. C = 72·7; H = 4·7.

0·0683, in 18·94 glacial acetic acid, gave $\Delta t = -0{\cdot}066^{\circ}$. M.W. = 213.
0·0693, „ 17·63 „ „ „ „ $\Delta t = -0{\cdot}068^{\circ}$. M.W. = 225.
0·0531, „ 17·85 „ „ „ „ E = 0·032. M.W. = 235.
$C_{13}H_{10}O_3$ requires C = 72·9; H = 4·7 per cent. M.W. = 214.

The substance was readily soluble in hot glacial acetic acid, but much less so in the cold acid, crystallising on cooling in bright yellow needles or plates. The solutions were bright yellow, with a green fluorescence. It was slightly soluble in benzene, almost insoluble in alcohol or acetone, and insoluble in water, chloroform, light petroleum, or ether. It was soluble in dilute alcoholic potash, forming a red solution from which it could be reprecipitated in a somewhat impure form by hydrochloric acid. A suspension of the substance in water was neutral to litmus, but addition of ferric chloride gave a red colour, which was not discharged by dilute hydrochloric acid. It was insoluble in aqueous alkalis, and it did not react with benzoyl chloride, so that hydroxyl groups would appear to be absent. It dissolved on warming with 75 per cent. sulphuric acid, forming a deep yellow solution with a green fluorescence, but the original substance could not be recovered by neutralising the acid. Some reaction had therefore taken place, probably the removal of a side chain.

As the yellow compound had a strong resemblance to certain naphthalene derivatives discovered by Collie (Trans., 1893, **63**, 329; 1896, **69**, 293), an attempt was made to prepare the parent hydrocarbon. Owing to the small quantity of material available, distillation with zinc dust did not offer much prospect of success, and electrolytic reduction was therefore tried. The solution of the substance in sulphuric acid was diluted until the strength of the acid was about 25 per cent., and was placed in a porous pot, together with a cathode of platinum gauze, which could be rapidly rotated. To prevent formation of oxidising substances, an amalgamated zinc plate was used for the anode, a slow stream of 25 per cent. sulphuric acid being made to flow through the anode vessel to remove the bulk of the zinc which dissolved. The current density was about 0·1 ampere per sq. cm. After electrolysis had proceeded for some hours, the cathode solution was shaken with benzene, and, on evaporation of the latter, a minute quantity of a colourless substance, melting at 96—97°, was obtained. The yield could not be improved. Substitution of a zinc cathode for the platinum gave only oily substances, which could not be caused to crystallise, and which were too small in quantity for effective distillation.

A suspension of the substance in carbon tetrachloride decolorised a solution of bromine in the same solvent. A crystalline substance appeared to be formed at first, but it dissolved on further addition of bromine. On shaking the mixture with water, hydrobromic acid could be detected in the latter. In the quantitative experiments weighed quantities of the substance were shaken with a moderate excess of bromine solution, and, when the substance had completely dissolved, the excess of bromine was determined by means of potassium iodide and thiosulphate in the usual way. The free acid was then found by titration with standard alkali. The bromine solution contained 0·0275 gram equivalent per litre and the alkali 0·0384 equivalent:

0·0707 gram required 25·64 c.c. bromine solution and 15·99 c.c. alkali.

Or 214 grams reacted with 2·13 equivalents of bromine, forming 1·86 equivalents of acid.

0·0757 gram required 26·37 c.c. bromine and 16·68 c.c. alkali.

Or 214 grams reacted with 2·05 equivalents of bromine, forming 1·81 equivalents of acid.

The formation of nearly two equivalents of acid from two equivalents of bromine would seem to indicate the formation of an acid bromide, as in the reaction between bromine and keten (Trans., 1907, **91**, 1941), or in that between bromine and *cyclo*butan-1 : 3-dione described above, this acid bromide on addition of water giving one equivalent of hydrobromic acid and one of another acid.

The yellow compound was attacked by dilute permanganate in the cold, but only acetic acid could be detected among the products of oxidation. It also reacted with phenylhydrazine in glacial acetic acid, forming a compound containing nitrogen, which was insoluble in benzene but very soluble in alcohol, from which it could be crystallised in colourless needles or plates, melting sharply at 238°. A quantity sufficient for analysis could, however, not be obtained.

On treatment with an alkaline solution of hydroxylamine, an oxime was formed. The yellow compound was dissolved in a solution containing 10 grams of potassium hydroxide to 20 c.c. of water with 120 c.c. of alcohol. Excess of hydroxylamine hydrochloride dissolved in a little water was added, and the mixture was warmed for five minutes on the water-bath. On neutralising with hydrochloric acid, a yellow substance slowly separated, precipitation being complete in about two hours. It was washed with water and recrystallised from hot water. It was also soluble in alcohol. It melted and decomposed at 200° (corr.). The results of analysis seem to show that we did not succeed in getting this substance in a completely pure state; in fact, it could not be dissolved without showing signs of decomposition:

0·1072 gave 0·2336 CO_2 and 0·0576 H_2O. C=59·4; H=6·0.
0·1030 „ 0·2342 CO_2 „ 0·0517 H_2O. C=61·5; H=5·6.
0·1084 „ 0·2436 CO_2 „ 0·0555 H_2O. C=61·3; H=5·7.
0·1126 „ 9·98 c.c. N_2 (moist) at 18·5° and 761·6 mm. N=10·2.
I. $C_{13}H_{12}O_3N_2$ requires C=63·9; H=4·9; N=11·5 per cent.
II. $C_{13}H_{14}O_4N_2$ „ C=59·5; H=5·3; N=10·7 „

Formula I results from the reaction of hydroxylamine with two :CO groups according to the equation:

$$C_{13}H_{10}O_3 + 2NH_2{\cdot}OH = C_{13}H_{12}O_3N_2 + 2H_2O.$$

Formula II represents the reaction of two molecules of hydroxylamine, one reacting normally with a :CO group, and the other adding on to a double bond:

$$C_{13}H_{10}O_3 + 2NH_2{\cdot}OH = C_{13}H_{14}O_4N_2 + H_2O.$$

The aqueous solution of the hydroxylamine compound was acid to litmus. It was titrated with standard alkali containing 0·0384 equivalent per litre:

0·0777 gram required 6·23 c.c. alkali.

That is, 244 grams $C_{13}H_{12}O_3N_2$ require 0·75 equivalent of alkali, and 262 grams $C_{13}H_{14}O_4N_2$ require 0·81 equivalent of alkali.

It will be seen from the foregoing that so far we have found no clue to the constitution of the yellow condensation product of *cyclo*butan-1 : 3-dione, and the yield in the preparation of the substance and of all its derivatives is so poor that very much larger quantities of the raw material (that is, of *cyclo*butan-1 : 3-dione) than have been hitherto available would be required before this portion of the research could be resumed with any chance of success.

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CCXI.—*The Viscosity of Salt Solutions.*

By Malcolm Percival Applebey.

The changes in viscosity produced when salts are dissolved in water have been the subject of many important researches since Poiseuille's classical work on the flow of liquids in capillary tubes. The results obtained by the earlier workers in this field may be summarised as follows:

(1) The effect of salts on the viscosity of water is small, but generally positive. Some salts, however (for example, potassium chloride), diminish the viscosity of water.

(2) The effect of salts in increasing the viscosity increases more

rapidly than the concentration; the salts which diminish the viscosity have, however, less effect as concentration increases. A minimum value is reached at a certain concentration. The addition of more salt then raises the viscosity.

(3) The effect of a salt in increasing the viscosity of water is additively composed of a factor expressing the effect of the cation and a factor expressing the effect of the anion, when the solution is sufficiently dilute.

(4) The temperature-coefficient of the viscosity of a dilute salt solution is approximately equal to that of water.

These researches were necessarily confined to concentrated solutions, since the methods used were not of sufficient accuracy to measure the small changes in viscosity produced by small quantities of dissolved salt. It should also be noted that the earlier work is vitiated by the fact that the authors did not investigate the behaviour of their apparatus with respect to Poiseuille's law, but always assumed its rigid validity. The velocity of flow in the viscometers used was always greater than the limiting velocity at which eddying begins, and above which Poiseuille's law is not rigidly obeyed. The error thus caused in the determinations cannot be calculated from the data given.

Within recent years attention has been directed to the phenomena of viscosity in dilute solutions. The work of Kohlrausch (*Proc. Roy. Soc.*, 1903, **71**, 338) and that of Bousfield and Lowry (*Phil. Trans.*, 1905, **204**, *A*, 253) has shown the importance of studying changes of viscosity for the interpretation of the results obtained in conductivity determinations. The application of Stokes' theorem to strong electrolytes has made the knowledge of the viscosity effect of salts in dilute solution of great importance in the measurement of ionisation and the application of the dilution law to these solutions. The advance in the accuracy of relative viscosity determinations necessary for the investigation of these problems was secured by the important work of Grüneisen (*Wiss. Abh. Phys.-Tech. Reichs.*, 1905, **4**, 151). The theory of the viscometer was very thoroughly investigated by him, and methods of standardisation were developed which enabled him to determine the deviation of any viscometer used from the simple Poiseuille law. His experiments were all corrected for this deviation, and furnish the first accurate determinations of viscosity in dilute solutions.

Investigations have also been carried out by Hosking (*Phil. Mag.*, 1904, [vi], **7**, 469), who has studied the effect of temperature and concentration over wide limits for lithium chloride, whilst Bousfield and Lowry (*Phil. Trans.*, 1906, **206**, *A*, 101) have also made some observations on dilute solutions.

The work of Grüneisen is remarkable for the discovery of a general phenomenon which the less exact methods of earlier workers had not revealed. He has shown that the viscosity-concentration curve for all salts has a change of curvature at the dilute end in the sense that the first particles of salt added to water have a greater effect in increasing, or a less effect in diminishing, the viscosity of water than subsequent additions. The change of curvature is scarcely noticeable unless the curve is plotted on a very large scale. A much more convenient method is to plot the differential quantity:

$$\frac{\text{Relative viscosity} - 1}{\text{Molecular concentration}}.$$

against the cube-root of the concentration as recommended by Grüneisen.

This change of curvature was observed by Grüneisen with every member of a large series of salts investigated by him. No such effect has ever been found in solutions of non-electrolytes. It is not surprising therefore that Grüneisen has endeavoured to connect the phenomenon with ionisation. The following formula given by him corresponds with the observations with fair accuracy over a considerable range:

$$\frac{\eta/\eta_0 - 1}{m} = A\alpha + B(1-\alpha) + Cm,$$

where η/η_0 = relative viscosity,
m = molecular concentration,
α = degree of ionisation,
and A, B, and C are constants.

The present work was undertaken with the following objects:

(1) To carry the investigations to greater dilutions than Grüneisen reached, and thus to test his formula;

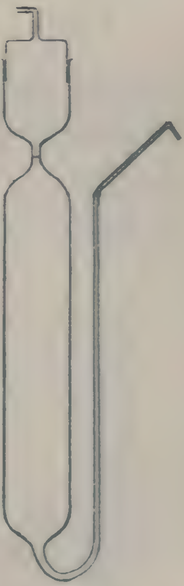
(2) To determine the effect of temperature, especially in dilute solutions; and

(3) To investigate the connexion between the viscosity of a solution and its molecular and ionic conditions.

Materials.—It was thought advisable to investigate thoroughly some one salt over wide ranges of temperature and concentration. Lithium nitrate was chosen, as its high solubility permits the investigations to be carried to very high concentrations. It was obtained either from Kahlbaum or from Merck in the form of crystalline lumps with an indefinite amount of water of crystallisation. It appeared to be a mixture of the two hydrates, $LiNO_3,\frac{1}{2}H_2O$ and $LiNO_3,3H_2O$, described by Donnan and Burt (Trans., 1903, **83**, 335). It was recrystallised before use in the form of the trihydrate. A spectroscopic examination showed no impurities except a trace of sodium. The water used was conductivity water free from dust. The dissolved air was removed by exhaustion in the cold just before use. This precaution is necessary to prevent the appearance of air-bubbles in the apparatus during determinations.

Preparation of Solutions.—The anhydrous salt is extremely hygroscopic, and very prolonged heating is necessary to bring it to a constant weight. The making up of solutions by weight is thus a very tedious process. It was therefore decided to determine the concentration of the solutions used by means of a previously determined density curve at 25°. The dehydration of the salt for this purpose did not present such difficulties, as less of the salt was necessary for a determination. The labour was also much lessened by the use of a specimen crystallised at about 70°, which was practically anhydrous. An appropriate weight of the salt was dehydrated by heating it for at least twenty-four hours in a small platinum crucible in an air-bath heated by boiling aniline. The crucible was allowed to cool in a desiccator, and then weighed in a stoppered glass bottle. The correct weight of water was then weighed into a wide-mouthed stoppered bottle, and the crucible dropped in.

FIG. 1.



Density Determinations.—The determinations at 25° and 18° were made in U-shaped pyknometers of test-tube glass, holding about 10 c.c. Each pyknometer was weighed against a counterpoise, and the results were corrected for displaced air. The density of each solution was determined with two separate pyknometers.

On account of the expansion of the solution before weighing, these pyknometers could not be used at 0°. The form shown in Fig. 1 was used for this temperature. The pyknometers used held about 20 c.c. The results usually agreed to 0·00002, although the agreement was not always so good at 0°. This is due, in part, to the difficulty of temperature regulation, and in part to the contamination of the ground surface, in which the stopper fits, with solution in some experiments. Simple wiping with a filter-paper (the usual method of cleaning the open end of a pyknometer) fails to remove this. The error might have been avoided if the stopper had been ground on outside instead of inside the open end of the pyknometer. For the purpose of viscosity determinations, however, an accuracy of 0·0001 is amply sufficient at 0°, and the errors were never so large as this.

The densities determined at 25·01° are given in table I. The following equation was found to express the results with sufficient exactness to justify its use for calculating concentrations:

$$m = 25{\cdot}103\ (s - s_0) - 16{\cdot}337\ (s - s_0)^2,$$

where s = density of solution,

s_0 = density of water,

m = concentration expressed in gram-molecules per 1000 grams of solution.

The degree of accuracy obtained in determining concentrations in this manner may be seen by the second column of table I.

TABLE I.—*Density of solutions of lithium nitrate at* 25·01°.

		$D^{25·01°}_{4°}$		
Concentration.	Concentration calculated from equation.	Pyknometer I.	Pyknometer II.	Mean density.
0·0	0·0	—	—	0·99707
0·1296	0·1296	1·00225	—	1·00225
0·1378	0·1388	1·00262	1·00263	1·00262
0·1458	0·1463	1·00293	1·00291	1·00292
0·1571	0·1577	1·00338	1·00338	1·00338
0·1724	0·1722	1·00396	—	1·00396
0·1971	0·1981	1·00500	1·00500	1·00500
0·2137	0·2144	1·00565	1·00567	1·00566
0·3145	0·3137	1·00967	1·00970	1·00969
0·3255	0·3238	1·01008	1·01008	1·01008
0·3605	0·3606	1·01158	1·01155	1·01157
0·3905	0·3899	1·01275	1·01277	1·01276
*0·4248	0·4016	1·01325	1·01325	1·01325
0·4851	0·4855	1·01664	1·01668	1·01666
0·6066	0·6061	1·02160	1·02163	1·02161
0·8283	0·8281	1·03077	1·03082	1·03080
0·9059	0·9050	1·03400	1·03402	1·03401
*0·9960	0·9861	1·03741	1·03741	1·03741
1·0968	1·0960	1·04206	1·04205	1·04205
1·2763	1·2752	1·04967	1·04967	1·04967
1·8639	1·8633	1·07529	1·07527	1·07528
2·2027	2·2020	1·09047	1·09047	1·09047
2·4602	2·4591	1·10223	—	1·10223
3·4086	3·4083	1·14759	1·14758	1·14759
*5·876	5·849	1·28344	1·28340	1·28342

The three solutions marked with asterisks show divergences considerably greater than the errors in determining the increase in density. In all three cases the concentrations calculated from the densities are smaller than those calculated from the weighings. It is most probable that the salt used in these experiments was not fully dehydrated. These values have been omitted in calculating the constants of the equation.

The densities at 18° and 0° are given in tables V and VI. The values at 18° agree very well with those determined by Kohlrausch and used by Grüneisen. The density determined by Perkin (Trans., 1893, **63**, 68) for a 2·63 weight-normal solution (=18·17 per cent.) at 25° is, however, considerably higher than that read off my curve.

Viscosity Determinations.—The use of viscometers of the Ostwald type in the measurement of relative viscosity depends on the validity of the law of Poiseuille, which is expressed by the equation:

$$\eta = \frac{\pi p r^4 t}{8lV},$$

where η is the coefficient of absolute viscosity,
p is the mean pressure producing flow,
V is the volume of liquid which flows through the capillary in the time t,
r is the radius, and
l the length of the capillary.

Since r, l, and V are constants depending only on the dimensions of the viscometer, the relation:

$$\eta = pt \times \text{constant}$$

should hold good for different liquids in the same viscometer, and if experiments are carried out with the same liquid flowing under different pressures, the product pt will have a constant value when the viscometer obeys Poiseuille's law.

Grüneisen (*loc. cit.*) has shown that this condition is by no means rigidly fulfilled by viscometers of the Ostwald type acting under their own hydrostatic pressure. He has found that the variation of pt is due to the fact that above a certain limiting velocity the flow of liquid in the viscometer is not steady, but that some of the potential energy is expended in forming eddies within the liquid. Hence the liquid is not forced down the capillary so quickly as it should be if Poiseuille's law held good, that is, t is greater than demanded by the simple law, and in consequence pt has a greater value than the constant found with slow flow.

Thus the phenomena of flow under varying pressures may be summarised as follows. When the pressure is small and the time large, pt is constant; on increasing the pressure and diminishing the time, a point is reached where eddy-formation begins. Beyond this point pt continually increases, and Poiseuille's law no longer holds. The readings of a viscometer are only trustworthy when the time of flow is so large as to ensure that the product pt remains constant (for the same liquid) over the whole range of variation in time of flow to be observed in the actual determinations. Grüneisen has tested several viscometers in a manner similar to that to be described later, and has published (*loc. cit.*) the pt-t curves obtained. He has then calculated a correction for the variation in *pt* over the region of his experiments, and applied this throughout his work.

It was thought possible to construct viscometers in which this correction should be negligible by reducing the velocity of flow considerably below the limits attained by Grüneisen.

This diminution in velocity of flow may be secured in three distinct ways:

(*a*) By reducing the diameter of the capillary.

(*b*) By lengthening the capillary.

(*c*) By reducing the hydrostatic pressure in the viscometer by bringing the two bulbs as near together as possible.

(*a*) Some experiments were tried with viscometers constructed with very fine capillaries. It was found, however, that the results were almost invariably vitiated by dust. The final form of viscometer adopted had a capillary radius of about 0·2 mm.; thus my tubes were considerably smaller than Grüneisen's, the radius of which varied between 0·34 and 0·48 mm.

(*b*) and (*c*) To lengthen the capillary in the ordinary Ostwald type of viscometer is to increase the pressure proportionally. The form shown in Fig. 2 was therefore adopted.* The bulbs cannot be brought nearer together than a certain limiting distance depending on the capillary rise in the viscometer; otherwise the liquid never falls below the lower mark. In the viscometers used, the lower mark was etched very near to the bulb where the capillary was slightly enlarged. At the completion of the experiment, the meniscus came to rest a few millimetres below the mark. The dimensions of the viscometers finally adopted were:

Radius of capillary	0·2 mm.
Length of capillary	11 to 22 cm.
Volume of bulb..............................	7 c.c. (approx.).
Mean difference of level	10·8 cm. (approx.).

How far the results given by any particular viscometer are vitiated by eddy-formation also depends on the amount of irregularity in the capillary (and especially at the ends of the capillary, where the flow suddenly changes). In the construction of a viscometer anything approaching a sudden change of diameter should be avoided. The junction of capillary and bulb should have the form of a smooth cone, as shown in Fig. 2.

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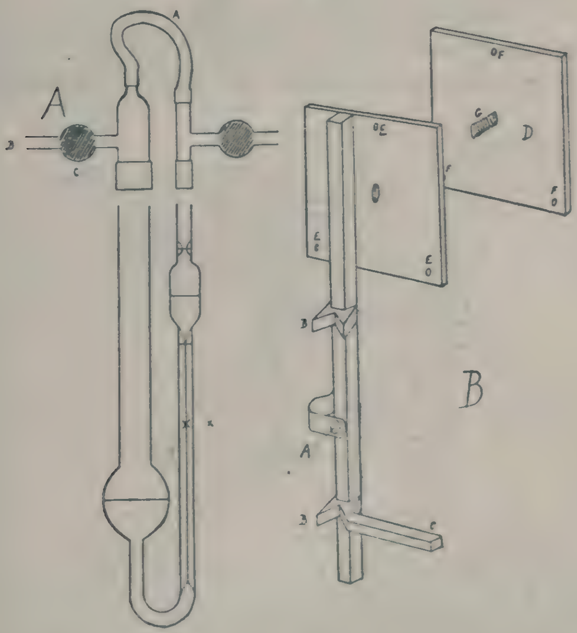
* The same object has been attained by Grüneisen by winding the capillary in a spiral. This method is, however, open to the objection that much of the energy which should be expended in driving the liquid on is used in changing the direction of flow as the capillary bends. This results in a very high value for the Grüneisen eddy-correction. Since it was hoped to avoid the Grüneisen correction altogether no experiments have been performed with spiral capillaries.

Standardisation of Viscometers.—Although from the dimensions of the viscometers it was probable that Poiseuille's law would be obeyed within the limits of experimental error, it was necessary to carry out special tests so as to be certain that irregularities in the glass were not present of such magnitude as to produce eddies and thereby cause the viscometers to disobey the simple law. The method here described is similar to that used by Grüneisen. In order to test a viscometer, it is necessary to observe its time of flow under varying pressures when filled with water, and to investigate the variation of the product pt. The pressure in any particular experiment is the sum of the external pressure applied and the hydrostatic pressure due to the head of liquid in the viscometer. The latter varies during the experiment, and an average value has to be found in the following way.

FIG. 2.

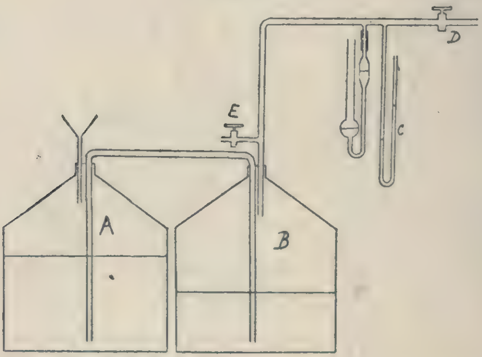


First, the small arm of the viscometer is attached to a water manometer, and the pressure directly read off by means of a reading-telescope and scale, together with the level at which the water stands in the viscometer. This determination is repeated for several different positions of the liquid in the viscometer, and a curve is drawn representing the variation in pressure head as the liquid falls in the viscometer. Secondly, by means of the reading-telescope, the time necessary for flow from the upper mark to known distances below the mark is measured. By combining these curves, namely, variation of pressure with depth and variation of time with depth, a curve is drawn which shows the variation of pressure with time throughout the whole tube. From this a value is obtained for the average hydrostatic pressure during flow. This is usually approximately equal to the pressure at mean time, but differs from that calculated from the difference of level at mean time owing to surface effects; for example, in one viscometer:

Mean hydrostatic pressure	10·60 cm. of water at 25°
Pressure at mean time	10·55 ,, ,, ,,
Difference of level at mean time...	10·99 ,, ,, ,,

The difference between the first and third of these numbers measures the surface-tension effect, and will be considered later.

FIG. 3.



The times of flow have now to be measured when a known excess of pressure is applied at the small arm of the viscometer. For this purpose it is necessary to have an arrangement capable of exerting a small pressure, which shall keep quite constant during the experiment. I have found the apparatus shown in Fig. 3 to work very satisfactorily. The vessels *A* and *B*, which contained water, were so large that the movement of the air into the bulb of the viscometer during flow made no measurable alteration in the difference of level in *A* and *B* measured by the water manometer *C*. The pressure of the air in *B* remained constant to 0·1 mm. of water during the experiment when the cork of *B* and the rubber connexions were painted with celluloid varnish so as to prevent leakage. The pressure in *B* can be varied by allowing air to escape from *D* or by forcing in air with a bicycle-pump at *E*. The range of pressures under which experiments were performed was −1 to +20 cm. of water. The pressures were measured on the water manometer *C*, which could be read to 0·1 mm. by a reading-telescope.

The following table gives the values obtained with a satisfactory tube:

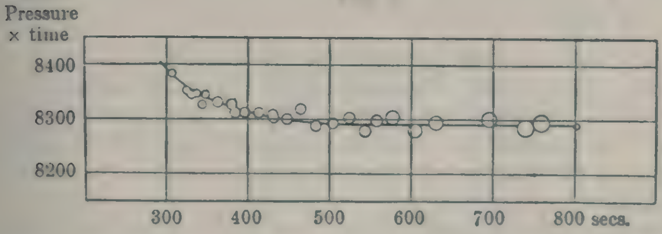
TABLE II.

Viscometer *R*. Hydrostatic pressure = 10·36 cm. of water at 25°.

Total pressure.	Time of flow in secs.	Pt.
10·36	800·2	8290
10·94	758·4	8297
11·205	739·5	8286
11·93	695·8	8301
13·15	630·8	8295
13·69	605·0	8282
14·38	577·5	8304
14·85	558·8	8298
15·23	543·6	8279
15·83	524·6	8304
16·47	503·6	8294
17·14	483·6	8289
17·85	466·0	8318
18·54	447·6	8299
19·19	432·6	8302
19·26	431·4	8309
20·09	413·7	8311
20·96	396·5	8311
21·61	384·6	8311
21·865	380·8	8326
22·89	363·9	8330
23·94	348·5	8343
24·20	344·0	8325
24·75	337·2	8346
25·20	331·1	8344
25·68	325·2	8351
25·94	321·7	8345
27·27	307·4	8383

These values are plotted in Fig. 4; the radius of the circles represents the experimental error of the determinations. The values of *pt*, although varying considerably, do not, at low pressures, differ by more than the experimental error. At higher pressures, *pt* rises above its normal value, the increase becoming rapid as the pressure increases. The experimental error in standardising is unfortunately much greater than that of the viscosity determinations. It is thus not quite certain that the tube obeys Poiseuille's law with the necessary accuracy. The following facts, however, indicate that the assumption is justifiable:

FIG. 4.



(1) Within the attainable limits of accuracy of standardisation no deviation from Poiseuille's law can be detected until the time of flow falls well below the minimum time of flow in the actual determinations.

(2) The times of flow of any pair of tubes filled with water were in the same ratio as the times of flow for any solution determined. This shows that either the tubes obey the law rigidly, or that they all deviate to the same extent.

(3) The velocity of flow in the capillaries of my viscometer is only about one-fifth of that prevailing in Grüneisen's experiments. The correction applied by him for deviation from Poiseuille's law is only 0·045 per cent. for a normal solution of lithium nitrate. It is therefore probable that the deviation of my tubes from Poiseuille's law is not more than 0·01 per cent., and is consequently negligible for solutions less concentrated than normal.

Time.—This was measured by means of a carefully tested stop-watch, which was always in a constant state as regards winding at the beginning of each determination (the watch was always wound to its fullest extent half an hour before filling the viscometer). In the later experiments an electromagnetic device was used to start and stop the watch. The error in time determinations with a stop-watch is not greater than 0·2 sec., and with a large number of determinations the error of the mean result is not more than 0·1 sec. This is an error of 1 in 8000 at its maximum. In view of the magnitude of the other errors of the determinations, particularly the temperature effect, since with water a difference of 0·005° at 18° produces a change of 0·2 sec. in the time of flow of the quickest tube used, it seemed useless to attempt any more accurate determination of time.

Cleaning.—As the deposition of the least particle of solid in the capillary introduces errors far larger than the variations in viscosity which the viscometers were designed to measure, it is of the greatest importance to clean the tubes thoroughly after each determination with water containing no solid matter in solution or suspended.

In this research, conductivity water made by distillation in a closed apparatus (Hartley, Campbell, and Poole, Trans., 1908, **93**, 428) was used for washing the tubes. Before use it was carefully examined to see whether it contained any solid matter.

The conductivity of water gives no certain indication of its suitability for this purpose, for the conducting impurities remaining in a sample of good, distilled water are volatile (carbon dioxide and ammonia) and have no effect in the viscometer, whilst, on the other hand, organic impurities or suspended solids render the water useless, although their presence is not indicated by conductivity determinations. Consequently those samples of water which showed no suspended solid were chosen rather than those with a low conductivity. The average conductivity of the water used was about 1×10^{-6} mho at 18°. The water was quite free from organic impurities.

In spite of all precautions, the tubes frequently became contaminated with dust. When this happened, the tube was charged with a few c.c. of nitric acid and one drop of alcohol, and left overnight.

The presence of dust is betrayed by (1) the irregularity of the results; (2) the failure of the tube to give the same time of flow for water after washing and drying.

After cleaning, the tube is dried by gentle heating, while a current of air, freed from dust by passage through cotton-wool, is drawn through it.

Filling.—The viscometers are filled by pipettes of such content as to fill them from the middle of the upper to the middle of the lower bulb. With this arrangement the alteration of hydrostatic pressure due to small variations in the volume filled in by the pipette is a minimum. The liquid (and, if necessary, the pipette) to be used is first brought to the temperature at which the experiment is to take place. The error of the pipettes was measured by weighing successive fillings of water. The greatest variation in six fillings of an 8·7 c.c. pipette was 0·0022 c.c. Since the average diameter of the lower bulbs of the viscometers at their widest parts was 3·8 cm., the greatest error occasioned by variations in the volume of liquid delivered by the pipette will be

$$\frac{0{\cdot}0022}{1{\cdot}9^2 \times \pi} = 0{\cdot}000194 \text{ cm.}$$

in the head of liquid, and since the average head is 10·6 cm. of water, the error so occasioned is only 0·002 per cent., which is considerably less than the errors in determining the times of flow. The use of a pipette for filling the viscometer is therefore justified.

When filled, the viscometer is fitted with the apparatus shown in Fig. 2 (*A*), the object of which is to allow the liquid in the viscometer to be forced up the capillary, and to run down without contact with dusty air. The liquid is forced up by pinching the rubber tubing *A*, and applying pressure by means of a small hand-bellows at *B*. The air which enters is freed from dust by a tight cotton-wool plug in *C*.* When the liquid has risen above the upper mark, the tube *A* is released, and the air pressure equalises itself on the two sides of the viscometer. During the actual experiment no air from the outside enters. The friction of the air in *A* was found to be negligible.

As it is of great importance that the viscometer should be fixed rigidly and always in exactly the same position, a special holder was designed [Fig. 2 (*B*)]. The viscometer is fixed by means of the screw *A* with its wider arm resting in two V grooves *B*, *B* and a cross (× in Fig. 2) etched on the capillary, resting upon a line scratched on the side-piece *C*. The whole apparatus, which is constructed of stout brass, is now fitted on the brass plate *D*, three steel points *E*, *E*, *E* fitting exactly into three conical holes *F*, *F*, *F*. The points being fitted, the two parts are fixed together rigidly by a nut which is screwed down on the screw *G*, which passes through a hole in the front plate. (The nut must not be screwed down too tightly, or the steel points may be distorted.)

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* When the liquid in the viscometer is hygroscopic, and in all low temperature experiments the air is dried before passing into *B*.

The back plate is firmly attached to a wooden cross-piece supported by two wooden uprights fixed firmly to the bench and supported by stays so as to be very rigid. The wooden parts were made of well-seasoned wood to avoid warping. With this apparatus the viscometer can be brought to exactly the same position for each determination.

Temperature.—Experiments were carried out at 25°, 18°, and 0°. For the experiments at 25° and 18° the viscometers were immersed in thermostats holding 30 to 40 litres of water, which was kept in rapid motion by a good stirrer. Constancy of temperature was secured by Lowry spiral regulators, gas heating being used for the 25° bath, electric for the 18° bath. No variation of temperature was ever observed on a thermometer divided into wide twentieths, which could be read to 0·005°. The 0° bath was a well-stirred mixture of crushed ice and water. It usually remained constant to 0·02° during an experiment. The results were calculated to 0° by the use of a temperature correction.

Method of Experiment.—The time of flow is found for pure conductivity water, viscometer and pipette are then dried, and the solution to be determined is filled in. The time of flow is then measured several times. Finally, the viscometer and pipette are again cleaned and dried, and the water value is again determined. This precaution is necessary, as the water values sometimes slowly increase during successive fillings, owing to contamination with organic matter or incomplete washings, and the change is so small as to escape notice in any other way. In most of the determinations performed in this research, the original and final water values agreed to 0·2 sec. In a few cases, where it was obvious by the appearance of a large and irregular water value after a constant solution value that contamination had occurred in the final water filling only, the original water value was used in calculation.

Calculation of Results.—The simple Poiseuille law gives:

$$\eta/\eta_0 = pt/p_0t_0,$$

where η = viscosity,
t = time of flow,
p = hydrostatic pressure in the tube, and
η_0, t_0, and p_0 are the corresponding values for water.

The average pressure producing flow is that of a column of water equal to the mean difference in level diminished by a quantity expressing the buoyancy of the air in which the experiment takes place, and by a quantity depending on the surface effects, proportional to the surface tension. This pressure has been determined in the course of standardising the tubes. It is equal to:

$$H(s_0 - \lambda) - K\gamma_0,$$

where H = mean difference of level,
s_0 = density of water,
λ = ,, ,, air,
γ_0 = surface tension of water,
and K = a constant depending on the form of the apparatus.

All the other terms in this expression being known, the constant can be evaluated.

The pressure for the liquid to be determined will be:

$$H(s - \lambda) - K\gamma.$$

The relative viscosity η/η_0 is therefore given by the expression:

$$\frac{H(s-\lambda) - K\gamma}{H(s_0-\lambda) - K\gamma_0} \cdot \frac{t}{t_0},$$

or

$$\frac{t}{t_0} \cdot \frac{H(s-\lambda) - K\gamma}{P(s_0-\lambda)},$$

where P is the hydrostatic pressure in cm. of water as measured in standardisation:

or

$$\frac{t}{t_0} \cdot \frac{s-\lambda}{s_0-\lambda} \cdot \frac{H - K\gamma/s}{P},$$

where the small correction λ is omitted from the surface-tension factor.

It is to be noted that no kinetic energy correction is to be applied in calculating the results of experiments with viscometers in which the capillary opens into a reservoir of the same liquid. The correction calculated by earlier observers (Hagenbach, *Pogg. Ann.*, 1860, **109**, 385; Finkener, see Gartenmeister, *Zeitsch. physikal. Chem.*, 1891, **6**, 524) is only applicable when the liquid flows from the capillary directly into the air. In viscometers of Ostwald type, however, the gain of kinetic energy at the beginning of the capillary is balanced by a loss of kinetic energy on emerging from the capillary into the lower bulb. The net increase of kinetic energy is therefore negligible, especially in viscometers of the slow-flow type described in the foregoing. Grüneisen has shown that the introduction of such a correction into the *pt* values in standardising a good tube entirely destroys the regularity of the results. I have therefore followed his practice, and omitted any correction for kinetic energy.

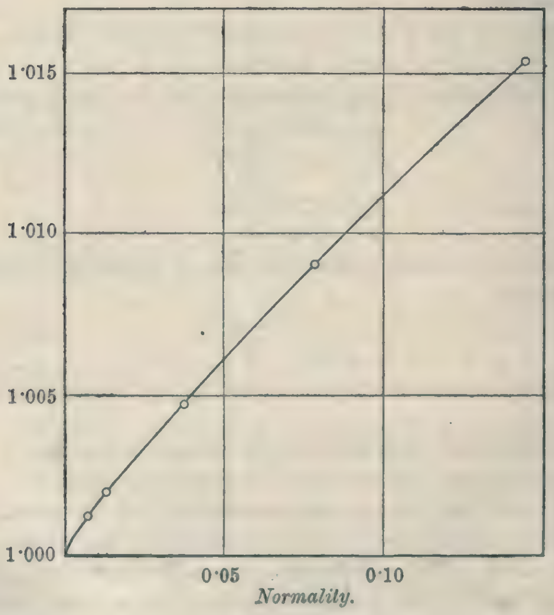
The times of flow for water in the viscometers used are given in the following table:

TABLE III.—*Times of flow for water (in seconds).*

Viscometer.	Time of flow at 25·01°.	Time of flow at 18°.	Time of flow at 0°.
4	1023·8	1207·7	2053·8
R	800·2	943·5	1604·4
S	703·6	830·3	1411·6
A	—	6013·9	—
B	—	7381·1	—

The slow tubes *A* and *B* were only used for very dilute solutions. Since the Grüneisen correction for these determinations would have been negligible, these tubes were not standardised. The viscosity determinations are given in tables IV, V, and VI. The viscosities of the solutions at 18° are calculated from the equation developed above.

FIG. 5.



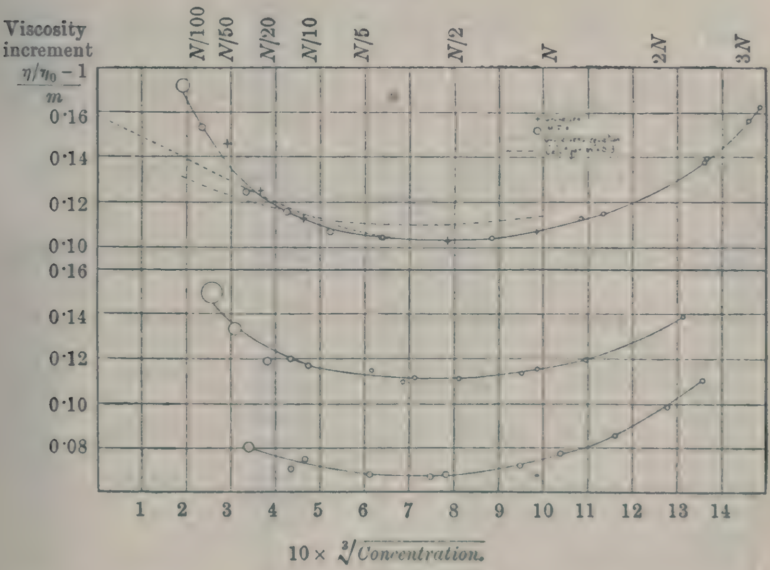
The surface tensions are interpolated from the values of

Gradenwitz (*Diss.* Breslau, 1902) and Piepenstock (*Diss.* Munich, 1908). These determinations were unfortunately only carried out at 18°. The introduction of the surface-tension correction into the results at 25·01° and 0° has therefore been impossible. At these temperatures the relative viscosities are calculated by the simple formula

$$\eta/\eta_0 = \frac{t(s-\lambda)}{t_0(s_0-\lambda)}.$$

For the purpose of comparison, the uncorrected viscosities at 18° are included in table V.

FIG. 6.



The viscosities of the more dilute solutions at 18° are plotted in Fig. 5, while the molecular viscosity increments at the three temperatures are given by Fig. 6. Fig. 6 also contains Grüneisen's values at 18° and the curve given by his equation:

$$\frac{\eta/\eta_0 - 1}{m} = A\alpha + B(1-\alpha) + Cm.$$

TABLE IV.

Viscosities at 25·01°.

$D^{25\cdot01^\circ}_{4^\circ}$ s.	Concentration m.	$10m^{\frac{1}{3}}$.	Viscometer.	Relative viscosity $\eta/\eta_0=\frac{(s-\lambda)t}{(s_0-\lambda)t_0}$.	Mean relative viscosity.	Viscosity increment $\frac{\eta/\eta_0-1}{m}$.
0·99777 0·99776	0·0174	2·59	S 4	1·00255 1·00265	1·0026	0·149
0·99824 0·99827	0·0299	3·10	S R 4	1·00405 1·00395 1·00395	1·0040	0·133
0·99933 0·99934	0·0567	3·84	R S 4	1·00675 1·0068 1·0066	1·0067	0·119
1·00035 1·00038	0·0825	4·355	S 4 S	1·00985 1·01005 1·0097	1·0099	0·120
1·00135 1·00135	0·1071	4·75	4 S R	1·01265 1·01245 1·01245	1·0125	0·1165
1·00642 1·00642	0·2333	6·155	R S 4	1·0264 1·0266 1·0271	1·0267	0·1145
1·01008 1·01008	0·3238	6·867	4 S	1·0356 1·03525	1·0354	0·1095
1·01159 1·01159	0·3643	7·142	4 S	1·0402 1·0408	1·0405	0·1111
1·01884 1·01882	0·5385	8·136	S R	1·0597 1·0598	1·05975	0·1110
1·03240	0·8666	9·533	4 R	1·0979 1·09805	1·0980	0·1131
1·03656 1·03660	0·9663	9·886	4 S R	1·1117 1·11145 1·1104	1·1112	0·1151
1·05134 1·05146	1·316	10·96	R S	1·1567 1·1567	1·1567	0·1191
1·09364 1·09365	2·2719	13·146	S R	1·31515 1·3151	1·3151	0·1387
1·17009 1·17006	3·8541	15·678	S R	1·74095 1·74055	1·74075	0·1922
1·20848 1·20833	4·578	16·60	4	2·0577	2·0577	0·2310
1·28344 1·28340	5·849	18·02	R 4	3·027 3·024	3·0255	0·346

TABLE V.

Viscosities at 18°.

$H = 10·99$, $P = 10·60$, $k = 0·39$.

$D_{4^{\circ}}^{25\cdot01^{\circ}}$.	Concentration m.	$10m^{\frac{1}{3}}$.	$D_{4^{\circ}}^{18^{\circ}} = s$.	Surface tension (relative to water) γ.	Viscometer.	Relative viscosity $\frac{\eta}{\eta_0} = \frac{t}{t_0} \cdot \frac{s-\lambda}{s_0-\lambda} \cdot \frac{H-K\gamma/s}{P}$	Mean relative viscosity.	Mean relative viscosity (uncorr.).	Viscosity increment (uncorr.).
[Solution made up by weight]	0·00724	1·93	0·99892	1·0004	*A* *B*	1·00122 1·00127	1·00124	1·00125	0·172
0·99760 0·99759 0·99758	0·0131	2·36	0·99916 0·99915	1·0007	*A* *B*	1·00200 1·00199	1·00260	1·00201	0·153
0·99858 0·99858	0·0379	3·36	1·00016	1·0014	*S* *R* 4 *A*	1·0047 1·0047 1·0047 1·00469	1·0047	1·0047	0·124
1·00019 1·00022	0·0784	4·28	1·00183 1·00183	1·0023	4 *S* *R*	1·00905 1·0089 1·0092	1·00905	1·0090	0·115
1·00285 1·00285	0·1446	5·25	1·00452 1·00453	1·0036	4 *S*	1·0156 1·0153	1·01545	1·01535	0·106
1·00771 1·00771	0·2653	6·43	1·00951	1·0061	4 *S*	1·0278 1·0278	1·0278	1·0276	0·104
1·02563 1·02562	0·7034	8·89	1·02769 1·02768	1·0151	4	1·0737	1·0737	1·0731	0·1039
1·05003 1·05001	1·283	10·87	1·05245	1·0273	*S* *R*	1·1441 1·1438	1·14395	1·1429	0·1113
1·05811 1·05806	1·471	11·37	1·06066 1·06061	1·0313	4 *S* *R*	1·1697 1·17015 1·1699	1·1699	1·16865	0·1147
1·10498 1·10498	2·528	13·62	1·10812 1·10812	1·0508	*S* *R*	1·3497 1·34995	1·34985	1·3472	0·1373
1·10644 1·10643	2·550	13·66	1·10959 1·10956	1·0512	*S* *R* 4	1·3579 1·3579 1·35795	1·3579	1·3552	0·1393
1·13341 1·13342 1·13343	3·120	14·61	1·13685	1·0618	*R*	1·4906	1·4906	1·48695	0·1561
1·14122 1·14120	3·279	14·86	1·14475 1·14475	1·0648	4 *R*	1·5366 1·53685	1·5367	1·5327	0·1624
1·1968 1·1970	4·363	16·34	1·2008 1·2010	1·0812	4 *R*	1·9346 1·9346	1·9346	1·9274	0·2125

TABLE VI.

Viscosities at 0°.

$D^{25\cdot01°}_{4°}$.	Concentration m.	$10m_{\frac{1}{3}}$.	$D^{0°}_{4°}$.	Viscometer.	Relative viscosity $\frac{\eta}{\eta_0}=\frac{(s-\lambda)t}{(s_0-\lambda)t_0}$.	Mean relative viscosity.	Viscosity increment $\frac{\eta/\eta_0-1}{m}$.
[Solution made up by weight]	0·0401	3·42	1·00161 1·00161	4 *R* *S*	1·0032 1·00325 1·0032	1·0032	0·080
1·00039 1·00038	0·0833	4·37	1·00347 1·00352	*S*	1·0058	1·0058	0·070
[Solution made up by weight]	0·1026	4·68	1·00447 1·00449	*R* 4	1·0077 1·00755	1·0076	0·074
1·00626 1·00626	0·2294	6·12	1·00990 1·00990	*R* 4	1·0156 1·0153	1·01545	0·0675
1·01391 1·01389	0·4179	7·48	1·01818 1·01815 1·01817	4 *S* 4 *R*	1·0278 1·0279 1·02775 1·0278	1·0278	0·0665
1·01650 1·01651	0·4818	7·84	1·02099	4 *R* 4	1·0324 1·03255 1·0326	1·0325	0·0675
1·03206 1·03203	0·8577	9·50	1·03775	*S* *R*	1·0616 1·0616	1·0616	0·0718
1·04364 1·04368	1·134	10·40	1·05021 1·05019	*R* *S* 4	1·0873 1·0875 1·08775	1·0875	0·0772
1·06247 1·06248	1·572	11·63	1·07040 1·07036	4 4 *S*	1·1344 1·1346 1·1344	1·1345	0·0855
1·08578 1·08583 1·08578	2·099	12·80	1·09505	4 *R* *S*	1·2067 1·20675 1·2066	1·2067	0·0984
1·10451 1·10451	2·508	13·59	1·11466 1·11453 1·11466	*R* *S* 4	1·2768 1·2771 1·2770	1·2770	0·1104

Discussion of Results.—The viscosities determined at 18° agree very satisfactorily with those obtained by Grüneisen. The values obtained for the most dilute solutions, however, differ considerably from those calculated from the formula proposed by him. The course of the curve given by Grüneisen's equation:

$$\frac{\eta/\eta_0-1}{m} = Aa+B(1-a)+Cm$$

is shown by the dotted line in Fig. 6. When $m=0$, that is, at infinite dilution, $a=1$ and $\frac{\eta/\eta_0-1}{m}=A$. The increment curve ought therefore to cut the axis of ordinates at a distance *A* from the origin. The value of *A* given by Grüneisen is 0·15868. The actual course of the increment curve is, however, quite different. The values obtained in the most dilute solutions are already much greater than this value, and the curve is still rising.

It may be noted that the most dilute point obtained by Grüneisen himself also lies considerably higher than the value calculated from his equation. Nor is this an isolated case. Out of ten salts investigated by him at sufficiently great dilution, in eight the most dilute solutions give values too high for his equation. The determination of $\frac{\eta/\eta_0 - 1}{m}$ for these dilute solutions involves a very large experimental error, as has been indicated by the size of the circles round the determined points in Fig. 6. The general nature of the phenomenon nevertheless precludes the view that these high values are due to errors of determination, for, if that were the case, the determinations should be equally distributed above and below the calculated curve.

These considerations, together with the determinations at greater dilutions than Grüneisen's, show that, although his equation represents the facts over a certain range, it is not valid for all concentrations.

Grüneisen's equation contains the assumption that the effects of ion and undissociated salt respectively are distinct and separable, and that each is in all cases proportional to the concentration of the component considered. The second assumption can only be true if the process of solution is simply a mechanical mixing.

There is general agreement among physical chemists that the process of ionisation in electrolytes is accompanied by combination between the ions and the water molecules. Since water is a highly associated substance and consists of a mixture of simple and polymerised molecules, the extraction of water molecules from the system by the ions of the salt must be accompanied by a readjustment of the water equilibrium, polymerised molecules breaking down in order to restore the equilibrium. The effect of the ions on the viscosity of the system is therefore twofold: (1) the simple mixture effect, increasing the viscosity by reason of the great size of the hydrated ions; (2) the effect on the water equilibrium.*

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* It should be noted that the effect of the salt on the water equilibrium does not involve a change in the equilibrium constant, but is simply a dilution effect similar to that observed by Dixon and Peterkin on diluting nitrogen peroxide with an inert gas (Trans., 1899, **75**, 613). Thus, if the concentrations of simple and polymerised molecules in pure water be c_1 and c_n and the addition of an ionised substance lead to the extraction of x simple molecules of water, the concentrations of simple and poly-

The disappearance of the maximum density phenomenon when salts are dissolved in water shows that the effect on the water equilibrium is a depolymerisation. This effect will therefore lead to a diminution of viscosity. The diminution will not, however, depend alone on the concentration of the ions, but also on the amount of polymeride present. The effect will thus slowly decrease with successive additions of salt.

Another factor of which we must not lose sight is the change in size of the solvent envelope round the ion, the amount of water combined with each ion becoming greater on dilution.

In the following pages an attempt has been made to deduce a theoretical connexion between the viscosity of a solution and the molecular and ionic phenomena involved in its formation.

It has been tacitly assumed in the above that viscosity is a direct function of molecular size. The general validity of this relation is established by the following facts:

(1) Liquids which are known to be highly associated have usually also a high viscosity. The following examples may be cited:

	Association Factor.*	Viscosity at 20°.†
Propyl alcohol	2·25	0·0223
*iso*Propyl alcohol	2·86	0·0243
$\alpha\beta$-Dihydroxypropane	(large)	0·4479
Glycerol	(very large)	10·69 (at 18·28°)‡
Ethyl alcohol	2·74	0·01202
Acetic acid	3·62	0·01232
Ethyl acetate	0·99	0·00451
Ethyl ether	0·99	0·00237

* Ramsay and Shields, Trans., 1893, **63**, 1089.

† Gartenmeister, *Zeitsch. physikal. Chem.*, 1891, **6**, 524.

‡ O. G. Jones, *Phil. Mag.*, 1894, [v], **37**, 451.

(2) The work of Heydweiller (*Wied. Ann.*, 1895, **59**, 193) on the viscosity of liquids at high temperatures. The viscosity of water diminishes much more rapidly than that of unassociated liquids when the temperature is raised from 0° to 50°. Above 50°, when the association is small, the rate of diminution is approximately the same as that of unassociated liquids.

---

merised molecules in the solution will be c'_1 and c'_n, where (neglecting the change of volume on solution)

$$c_1 + nc_n = c'_1 + nc'_n + x,$$

and

$$\frac{c_1{}^n}{c_n} = \frac{c'_1{}^n}{c'_n} = k,$$

from which it follows that, since x is a positive quantity,

$$\frac{c_1}{c_n} < \frac{c'_1}{c'_n},$$

or that the extraction of simple molecules by the salt leads to a diminution in the association of the water remaining.

(3) The effect of pressure on the viscosity of water (Cohn, *Wied. Ann.*, 1892, **45**, 666). An increase of pressure always brings about an increase in viscosity in the case of non-associated liquids. At low temperatures the viscosity of water, however, first diminishes with increase of pressure, reaches a minimum value, and then rises in the normal manner. Since the association of water is accompanied by an increase of volume, as is shown by the maximum density phenomenon, the effect of pressure must be to break down the associated molecules. The marked diminution in viscosity, which is superimposed on, and in the initial stages entirely masks, the normal effect of pressure, can only be occasioned by this diminution in molecular size.

(4) The effect of different ions on the viscosity of water is in the reverse order of their mobilities, for example:

Salt.	Viscosity of *N*/10-solution at 18°.	Mobility of cation.
* Lithium nitrate	1·0113	42·6
† Sodium ,, ...	1·0044	52·6
† Potassium ,, ...	0·9941	75·5
‡ Cæsium ,, ...	0·9933	78·8

* Applebey. † Grüneisen, *loc. cit.*

‡ Unpublished result kindly communicated by Mr. T. R. Merton.

There is much evidence to show that ions of small mobility are heavily loaded with water molecules, and are thus larger than the more mobile ions.

Since the ions in a salt solution are enclosed in a water envelope, it is probably justifiable to neglect the specific chemical difference between hydrated ion and water-molecule, and to assume a rigid connexion between mean molecular volume and viscosity. As the simplest assumption, it has been supposed that these quantities are directly proportional.*

The different molecular species present in a salt solution are:

(*a*) Simple water molecules, H_2O;

(*b*) associated water molecules, assumed to be triple, $(H_2O)_3$;

(*c*) ions, hydrated to an unknown extent, $Li^+ + xH_2O$, $NO_3^- + yH_2O$;

(*d*) undissociated molecules, possibly combined with water, $LiNO_3$;

(*e*) in strong solutions salt complexes, $(LiNO_3)_n$.

The two kinds of water molecule are in kinetic equilibrium with one another. Their proportions in pure water can be obtained from the association constant in the following manner:

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* Dunstan and Thole have shown that these quantities are approximately proportional for different organic liquids which are not associated (*Proc.*, 1907, **23**, 19).

Let a be the association factor for water at 18°.

c_1 „ „ concentration of single molecules H_2O in gram-molecules per litre.

c_3 „ „ concentration of triple molecules $(H_2O)_3$ in gram-molecules per litre.

Then
$$\frac{3c_3 + c_1}{c_3 + c_1} = a,$$
and $54c_3 + 18c_1 = 1000s$, where s is the density of water.

Then
$$(3 - a)c_3 = (a - 1)c_1, \text{ or } c_3 = c_1\frac{a-1}{3-a},$$
and
$$\frac{54(a-1)}{3-a}c_1 + 18c_1 = 1000s,$$
whence
$$c_1 = \frac{1000s(3-a)}{36a} \text{ and } c_3 = \frac{1000s\,(a-1)}{36a}.$$

Now for the equilibrium $(H_2O)_3 \rightleftharpoons 3H_2O$

we have
$$\frac{c_3}{c_1^{\,3}} = k,$$
whence
$$k = \frac{1296\,(a-1)a^2}{10^6s^2(3-a)^3}.$$

Taking at 18° Ramsay's value of 1·65 for the association constant (*Zeitsch. physikal. Chem.*, 1895, **15**, 106) and 0·99863 as the density, $k = 0{\cdot}0009347$.

The value of k thus found can be used to calculate the effect of the salt on the water equilibrium.

Taking a solution of weight normality m, density s, and degree of ionisation α,

1000 c.c. of the solution weigh $1000s$ grams.

Of this the salt accounts for Mms grams (where M = molecular weight of the salt), leaving $(1000 - Mms)$ grams of water.

Now, if w be the average hydration number for the two ions, that is, if 1 gram-molecule of the salt, completely ionised, combines with $2w$ molecules of water, the amount of water thus removed from the system is:

$$2m\alpha sw \times 18 \text{ grams.}$$

The free water is therefore reduced to:

$$(1000 - Mm - 36m\alpha w)s \text{ grams.}$$

Letting c_1 and c_3 as before represent the concentration of single and triple molecules, we have:

$$54c_3 + 18c_1 = (1000 - Mm - 36m\alpha w)s,$$

or, since $c_3 = k \times c_1^{\,3}$,

$$54kc_1^{\,3} + 18c_1 = (1000 - Mm - 36m\alpha w)s,$$

from which c_1 and c_3 can be obtained (most conveniently by trial).

The total number of gram-molecules in a litre of solution is:

$$c_1 + c_3 + ms(1 + \alpha).$$

The mean molecular volume is therefore:

$$\frac{1000}{c_1 + c_3 + ms(1 + \alpha)}.$$

The mean molecular volume in pure water is:

$$\frac{1000}{c'_1 + c'_3},$$

where c'_1 and c'_3 are the concentrations of single and triple molecules in pure water.

On the assumption that viscosity is proportional to mean molecular volume, we have therefore:

$$\frac{\eta}{\eta_0} = \frac{c'_1 + c'_3}{c_1 + c_3 + ms(1 + \alpha)}.$$

Owing to the absence of accurate determinations of several of the quantities involved in this treatment, and especially of the hydration numbers at different concentrations, it is at present impossible to submit the equation to a quantitative test. It may, however, be noted that the course of the calculated viscosity increment curve corresponding with the equation agrees with the actual form observed in one important respect. The calculated curve shows the phenomenon of a minimum increment at about 0·5 normal, as does the observed curve. As an illustration of this there has been included in Fig. 6 a curve representing the viscosity increment calculated on the assumption that the hydration of the ions is constant and equal to 6·3 molecules of water per ion. The curve has been calculated with Ramsay's value for the association of water at 18°, and with values of α obtained from Kohlrausch and Maltby's conductivity determinations (*Sitzungsber. K. Akad. Wiss. Berlin*, 1899, 655) by means of the relation:

$$\alpha = \frac{\lambda}{\lambda_\infty} \times \frac{\eta}{\eta_0},$$

where λ = molecular conductivity, and λ_∞ = molecular conductivity at infinite dilution.

The calculated curve differs considerably from the observed, although they are of the same general shape. A very inconsiderable change in hydration is, however, sufficient to bring the curves into harmony. The values of the hydration necessary have been found by trial, and are collected in the following table:

Normality.	Hydration calculated from viscosity in gram-molecules of water per gram-molecule of ion.
0·00724	8·0
0·0131	7·5
0·0379	6·5
0·0784	6·3
0·1446	6·1
0·2653	6·1
0·7034	6·05
1·0	6·05

These values are in good agreement with those obtained by other methods for various salts. For lithium nitrate itself Wymper (*Proc. Roy. Soc.*, 1907, **79**, 576) obtained a value of 13 for the hydration of a molecule of the salt in a normal solution (from the "neutral salt effect" in the inversion of sucrose). For potassium chloride in normal solution, Philip (*Trans. Faraday Soc.*, 1907, **3**, 145) gives 9·4, and Caldwell (*Proc. Roy. Soc.*, 1906, **78**, 290) 11 molecules of water per molecule of salt, whilst for more dilute solutions Bousfield (*Proc. Roy. Soc.*, 1904, **76**, 563) gives 12. In accordance with its smaller mobility, the lithium ion seems to be rather more hydrated than the potassium ion.

From the results obtained at 25·01°, the same method of calculation gives values for the hydration numbers about 0·3 higher than those obtained at 18°. A similar small increase of hydration with temperature is indicated by the conductivity values of many salts (Noyes, see Washburn, *Tech. Quart.*, 1908, **21**, 425).

For other salts, Grüneisen's values at 18° give:

Salt.	Normality.	Hydration in mols. per ion.
Sodium nitrate	0·1	3·4
	0·05	3·5
Lithium chloride	0·1	8·8

Salts which are less hydrated than these, however, give impossible values. Thus, potassium nitrate gives small, and cæsium nitrate larger, negative values. In view of these negative values, it may be recalled that Rennie, Higgin and Cooke (Trans., 1908, **93**, 1162) found that cæsium nitrate diminished the rate of solution of copper in nitric acid, whilst sodium nitrate and lithium nitrate greatly accelerated the action.

To sum up, this method of calculating the hydration, like the methods depending on the concentrating effect of neutral salts in chemical reactions, gives values approximating to the truth for substances which are much hydrated, but gives values too low for less hydrated substances. It is not improbable that the failure of all these methods of calculation in this respect depends on some hitherto unconsidered factor in the equilibrium of salt solutions which becomes of increasing importance as the hydration diminishes.

Summary.—1. It has been found possible to construct viscometers in which the flow of liquid is so slow that, for solutions whose viscosity differs little from that of water, Poiseuille's law is obeyed with an error of not more than one part in 10,000. The methods used in testing the viscometers are described.

2. A correction has been introduced for the variation in surface effects when different liquids are used in the viscometer.

3. Determinations of density and viscosity have been carried out with lithium nitrate solutions at 0°, 18°, and 25° over a large range of concentration.

4. The formula of Grüneisen is found not to represent the phenomena of dilute solution.

5. A method of calculating the viscosity of salt solutions from their hydration numbers, or vice versa, has been described. The application of this method to the viscosities of lithium nitrate solutions at 18° gives results consistent with the estimates of ionic hydration made by other observers.

6. The application of the method to other salts is discussed.

I am greatly indebted to Mr. D. H. Nagel and Mr. H. B. Hartley for much valuable advice and encouragement during the progress of this work.

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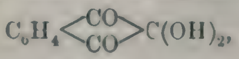
CCXII.—*Triketohydrindene Hydrate.*

By Siegfried Ruhemann.

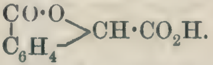
In a recent paper (this vol., p. 1438) it was shown that the condensation product of α-hydrindone with p-nitrosodimethylaniline, on treatment with dilute sulphuric acid, decomposes with the formation of triketohydrindene hydrate. Its formula was represented thus:



$$C_6H_4{<}\substack{CO\\CO}{>}C(OH)_2,$$

according to which the elements of water are united with the 2-ketonic group of triketohydrindene. There cannot be any doubt as to the correctness of this formula, because the union of water with any other ketonic group of the triketone would produce a coloured compound owing to the proximity of two ketonic groups, whereas triketohydrindene hydrate is colourless, as is also 1:3-diketohydrindene, $C_6H_4{<}\substack{CO\\CO}{>}CH_2$. Further evidence in support of the above formula is the fact that the hydrate, on treatment with phosphorus pentachloride, is transformed into the colourless 2:2-dichloro-1:3-diketohydrindene, $C_6H_4{<}\substack{CO\\CO}{>}CCl_2$. Triketohydrindene also forms additive products with other substances, such as guanidine or benzamidine, which are colourless, and therefore are to be represented by formulæ similar to that of triketohydrindene hydrate. The hydrate further reacts with hydrogen cyanide to yield the unstable cyanohydrin, $C_6H_4{<}\substack{CO\\CO}{>}C(OH)\cdot CN$.

A closer study of the remarkable behaviour of potassium hydroxide towards the hydrate which was described previously (*loc. cit.*, p. 1448) led to the following result. The reaction proceeds in three distinct phases, which are indicated by colour changes. On the addition of the alkali to the crystals of the hydrate, they turn yellow and then dissolve to form a yellow solution; this subsequently becomes blue, even at the ordinary temperature, if the alkali is concentrated. The blue colour, however, is very fugitive, and disappears on dilution with water to yield a colourless solution. On using dilute potassium hydroxide (about 15 per cent.), the blue colour does not appear unless the temperature is raised immediately after the addition of the alkali to the hydrate. The colourless alkaline solution, which represents the last phase of the reaction, contains the potassium salt of *o*-carboxymandelic acid, $CO_2H\cdot C_6H_4\cdot CH(OH)\cdot CO_2H$, because, on treatment with dilute sulphuric acid, it yields phthalidecarboxylic acid,

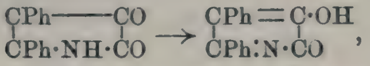


$$\begin{matrix}CO\cdot O\\ |\\ C_6H_4\end{matrix}{>}CH\cdot CO_2H.$$

The formation of this acid leads to the conclusion that, under the influence of the alkali, the five-carbon ring of triketohydrindene ruptures with the formation of phenylglyoxal-*o*-carboxylic acid, $CO_2H\cdot C_6H_4\cdot CO\cdot CHO$, which finally undergoes the change to phthalidecarboxylic acid. This behaviour resembles in every respect the change which, by the action of alkalis, phenylglyoxal undergoes to mandelic acid:

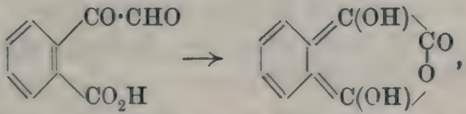
$$C_6H_5\cdot CO\cdot CHO \longrightarrow C_6H_5\cdot CH(OH)\cdot CO_2H.$$

The result arrived at in examining the behaviour of triketohydrindene hydrate towards potassium hydroxide supports the view which was expressed before (*loc. cit.*) concerning the product of the action of ammonia on the triketone. The formation of phenylglyoxal-*o*-carboxylic acid is to be regarded as the first change of the triketonic compound which is produced by the alkali, and this view follows, also, from the fact that the yellow alkaline liquor reduces Fehling's solution. The explanation of the intermediate phase of the reaction which is characterised by the blue colour of the alkaline solution is difficult, because the solution readily loses its colour, and passes into the final phase of the reaction. It is, therefore, only from analogy to the changes which the diketopyrrolines and the compounds with similar structure undergo, on treatment with alkalis, that a view can be expressed concerning the nature of the blue product. The blue solution which, for example, diketodiphenylpyrroline yields with potassium hydroxide was explained (Trans., 1909, **95**, 984) by the change into its tautomeric form:

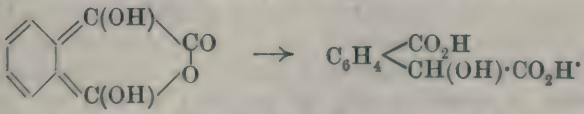


$$\begin{array}{l}\mathrm{CPh{-}{-}{-}CO}\\ \mathrm{CPh\cdot NH\cdot CO}\end{array} \rightarrow \begin{array}{l}\mathrm{CPh{=}C\cdot OH}\\ \mathrm{CPh{:}N\cdot CO}\end{array},$$

which contains a phenolic group and has an *o*-quinonoid structure. A similar arrangement may be assumed to exist in the potassium compound which is formed in the second phase of the action of the alkali on triketohydrindene hydrate. Accordingly, phenylglyoxal-*o*-carboxylic acid, which is first produced, undergoes ring formation, thus:



in which, also, phenolic groups are associated with an *o*-quinonoid structure. A substance with this constitution may be supposed to yield blue salts with alkalis. These, like the corresponding salts of the diketopyrrolines, are unstable, and, on dilution with water, are transformed into the salts of *o*-carboxymandelic acid:



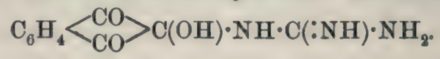
The further study of triketohydrindene hydrate led to results which appear to be of great interest. It was found that a deep blue colour is produced on warming a mixture of aqueous solutions of this compound and an aliphatic or an aliphatic-aromatic amino-acid which contains the amino-group in the side-chain. As shown below, this reaction has been successfully applied to a number of α-amino-acids, but as yet only two β-amino-acids have been tested, and they were found to differ markedly from the α-amino-acids in their behaviour towards the triketone, because with them the colour reaction takes place less readily, and in the case of β-amino-β-phenylpropionic acid is far less intense than with the corresponding α-amino-acids. No coloration, however, is produced by the triketone in solutions of aromatic amino-acids which contain the amino-group in the nucleus, nor does it occur with substituted amino-acids, such as phenylglycine or hippuric acid. On the other hand, triketohydrindene hydrate gives a blue reaction with peptone, and this fact in the light of the results indicated above leads to the conclusion that in the peptones, compounds occur which contain the free amino-group of amino-acids.

The same coloration is produced in normal human urine on warming it with an aqueous solution of the reagent. This behaviour agrees with the observations of Abderhalden and Pregl (*Zeitsch. physiol. Chem.*, 1905, **46**, 19; see also Abderhalden and Schittenhelm, *ibid.*, 1906, **47**, 1396), according to which the urine contains a protein-like substance. The authors showed that it does not contain free amino-acids, but that these are formed from it on hydrolysis.

EXPERIMENTAL.

Triketohydrindene hydrate was prepared in the manner described before (*loc. cit.*) by warming slightly the product of the action of *p*-nitrosodimethylaniline and α-hydrindone with dilute sulphuric acid; its extraction from the dark solution which is formed, is more conveniently effected by ethyl acetate than by ether on account of its greater solubility in that solvent.

Additive Product of Triketohydrindene with Guanidine,



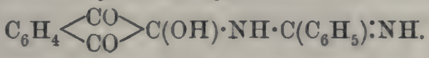
$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C(OH)\cdot NH\cdot C(:NH)\cdot NH_2.$$

This is formed by adding triketohydrindene hydrate (1 gram), dissolved in water, to an aqueous solution of guanidine, obtained from its chloride (0·6 gram) and the calculated quantity of potassium hydroxide. The mixture turns red and soon deposits a colourless solid, which is insoluble in water, alcohol or benzene; it does not melt, but begins to darken at about 190° and finally becomes black:

0·2015 gave 0·4045 CO_2 and 0·0740 H_2O. C = 54·75; H = 4·08.
0·1945 „ 32·6 c.c. N_2 at 20° and 754·5 mm. N = 19·02.
$C_{10}H_9O_3N_3$ requires C = 54·79; H = 4·11; N = 19·18 per cent.

On heating the compound with water for some time, slight decomposition takes place, and a small quantity dissolves to yield a red solution.

Additive Product of Triketohydrindene with Benzamidine,



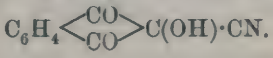
$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C(OH)\cdot NH\cdot C(C_6H_5){:}NH.$$

This is prepared in a similar way to the former substance, namely, by adding sodium carbonate to the mixture of triketohydrindene hydrate (1·2 grams) and benzamidine hydrochloride (1 gram) dissolved in hot water. A white solid is soon precipitated, which is insoluble in water; it is sparingly soluble in boiling alcohol, but does not separate from the solution without the addition of water, when colourless prisms are formed, which darken at about 200° and decompose at 229—230° with evolution of gas:

0·2011 gave 0·5050 CO_2 and 0·0805 H_2O. C = 68·49; H = 4·44.
0·2051 „ 17·8 c.c. N_2 at 17° and 762 mm. N = 10·10.
$C_{16}H_{12}O_3N_2$ requires C = 68·58; H = 4·29; N = 10·0 per cent.

This substance is insoluble in sodium carbonate; it is decomposed by hot potassium hydroxide with the formation of benzaldehyde.

Additive Product of Triketohydrindene with Hydrogen Cyanide,

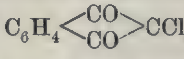


$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C(OH)\cdot CN.$$

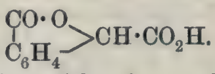
Whilst the additive compounds mentioned above are fairly stable, the *cyanohydrin*, which triketohydrindene hydrate forms with hydrogen cyanide, is readily decomposed. It is obtained by mixing the triketone hydrate (0·5 gram), dissolved in water, with potassium cyanide (0·5 gram), and then adding dilute hydrochloric acid to the deep red solution which is produced. The colour disappears and pale brown needles separate which sinter and darken at about 120°, and at 148° melt with evolution of gas. The compound dissolves in boiling water, but at the same time decomposes. For analysis, the crystals formed in the reaction were washed with cold water and dried in a vacuum desiccator over sulphuric acid:

0·2053 gave 13·8 c.c. N_2 at 18° and 749 mm. N = 7·64.
$C_{10}H_5O_3N$ requires N = 7·49 per cent.

Action of Phosphorus Pentachloride on Triketohydrindene Hydrate.

On mixing the triketone hydrate (1 mol.) with phosphorus pentachloride (2 mols.), no reaction takes place at the ordinary temperature; at 100°, the mixture evolves hydrogen chloride and assumes a red colour, which is probably due to the removal of water and the formation of triketohydrindene. The action proceeds more readily if phosphoryl chloride is used together with phosphorus pentachloride; on warming, the whole dissolves to yield a yellow solution, which is cooled and then poured on ice, when an oil is precipitated which soon solidifies. The solid is washed with light petroleum, which removes a yellow product, whilst a colourless substance remains undissolved. This is readily soluble in hot dilute alcohol, and, on cooling, crystallises in colourless plates. The yield is poor owing to the formation of the yellow by-product. The compound was identified as 2:2-dichloro-1:3-diketohydrindene,  $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}CCl_2$, by the melting point, 124—125°, and its chemical behaviour (compare Zincke and Gerland, *Ber.*, 1888, **21**, 2390).

Formation of Phthalidecarboxylic Acid from Triketohydrindene Hydrate.

The action of potassium hydroxide on the triketone hydrate was described in a previous paper (this vol., p. 1448) and more fully on p. 2026. It was stated that the final phase of the reaction yields a colourless solution. This, when treated with an excess of dilute sulphuric acid and digested on the water-bath for an hour, contains phthalidecarboxylic acid,  $\genfrac{}{}{0pt}{}{CO\cdot O}{C_6H_4}{>}CH\cdot CO_2H$. It is isolated from the acid solution by extraction with ether, and, on evaporation of the ether, is left as a white solid. This readily dissolves in hot water, and, on cooling, crystallises in colourless plates melting at 150—151°. The yield is almost theoretical. (Found: $C = 60{\cdot}70$; $H = 3{\cdot}37$. Calc., $C = 60{\cdot}67$; $H = 3{\cdot}37$ per cent.)

The compound is identical with the acid which Zincke (*Ber.*, 1894, **27**, 743), in the course of his researches on the action of bleaching powder on quinones, obtained from monochloro-β-naphthaquinone as well as from *iso*coumarincarboxylic acid.

Action of Triketohydrindenehydrate on Amino-acids.

On mixing a slightly warmed aqueous solution of triketohydrindene hydrate and glycine, an intense blue colour develops immediately, and, after a short time, a dark solid separates. The same behaviour is shown by all the α-amino-acids which I have been able to obtain; several of them I owe to the kindness of Dr. Hopkins, whom I have also to thank for the interest he took in the progress of the work. The reaction has been applied to alanine, valine, leucine, tyrosine, to α-amino-β-phenylpropionic, aspartic, and glutamic acids, to tryptophan and cystine. Owing to the fact that the latter compound is sparingly soluble in water, it must be boiled with a solution of the triketone hydrate; in all the other cases the reaction takes place almost with the same rapidity as with glycine, and requires mere traces of the reagents. The sensitiveness of the reagent is indicated by the fact that the blue colour is still perceptible on slightly warming glycine with a solution which contains 1 part of triketohydrindene hydrate dissolved in 15,000 parts of water. In the same dilution, the reagent yields with ammonia a yellow coloration, whereas the colour is red, or reddish-violet, on using more concentrated solutions (compare this vol., p. 1447). The shade of the blue coloration that is produced shows but slight variations with the different α-amino-acids. Of the β-amino-acids only two have been tested, namely, β-aminopropionic acid and β-amino-β-phenylpropionic acid. The latter, which was prepared according to Posner's directions (*Ber.*, 1903, **36**, 4313) by the action of hydroxylamine on cinnamic acid, differs remarkably from its isomeride, α-amino-β-phenylpropionic acid, in its behaviour towards triketohydrindene hydrate; no colour is produced on mixing the reagents dissolved in hot water. A faint violet coloration, however, develops if the solution is boiled for some time; on the other hand, the corresponding α-amino-acid readily reacts with the triketonic compound to yield a deep blue colour. The difference between α- and β-aminopropionic acids in their behaviour towards the reagent, although not so striking as with the former isomeric acids, is yet apparent, especially as regards the rapidity of the reaction, which in this case, also, is greater with the α-amino-acid. It is, however, necessary to examine a larger number of the β-amino-acids before, by means of the reagent, a general distinction between the two groups of amino-acids can be established. Neither phenylaminoacetic acid (phenylglycine) nor hippuric acid yield a coloration with the triketone hydrate, even on boiling the aqueous solutions of the mixtures, and this result indicates that the reaction depends on the amino-group of the amino-acid being intact. Aromatic amino-acids which contain the amino-group in the nucleus, for example, *o*-aminobenzoic acid, also do not respond to the test.

The chemical nature of the colour reaction has not yet been ascertained, but experiments in this direction are already in progress, and will be recorded shortly.

UNIVERSITY CHEMICAL LABORATORY,
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CCXIII.—*The Vapour Pressures and Molecular Volumes of the Mercuric Halides and the Relations between Atomic Volumes of Elements Before and After Combination.*

By Edmund Brydges Rudhall Prideaux.

The present investigation has the aim of comparing the volumes of liquid elements with those of their liquid compounds. As comparison temperatures the boiling points under atmospheric or other equal pressures have been retained. The results of Young and others show that at vapour pressures below one atmosphere it is a matter of indifference whether equal pressures or corresponding pressures are chosen for the above comparison. The procedure of finding atomic volumes at the boiling point is too well known to need description. It has been departed from in several particulars.

(1) No attempt has been made to tabulate difference of molecular volume, the ratios only being compared.

(2) No experimentally inaccessible atomic volumes, such as those of carbon and hydrogen, have entered into the calculation.

(3) The effect of structure on the molecular volume has been as far as possible eliminated by considering only simple compounds, in which there is not more than one multivalent element.

The term atomic or molecular volume at any pressure is used throughout to denote the total volume occupied by the gram-atom or gram-molecule liquid at such a temperature that its vapour pressure is that specified. Under these conditions the ratio between the specific volumes at, for example, 760 and 200 mm. pressure is a constant for liquids which are not associated or dissociated.

For example, $\frac{V_M(760)}{V_M(200)}$ is for C_6H_6 1·050, PCl_3 1·050, $C_2H_4Br_2$ 1·048, O_2 1·048, HCl 1·049. Instances could be multiplied.

Associated and monatomic liquids: H_2O 1·030, $CH_3{\cdot}CO_2H$ 1·041, Hg 1·012, A 1·014 (760—400), the normal value for this pressure interval being 1·028.

These relations may be connected in the following way with theories involving the conception of "co-volume." The term is used throughout as generally to mean the volume through which the molecules have motion relatively to one another, sometimes called "free ether," as distinguished from the "bound ether" or interatomic space, which, together with the volumes of the atoms themselves, makes up the "*b*" of van der Waals' equation (Clausius) which no other atom can penetrate.

Now, if we imagine an ideal and normal liquid expanding from the condition in which the co-volume is zero (which, as will be shown, is probably not in most cases $-273°$), the vapour pressure will increase at the same time, and since the pressure is a function of the temperature and the increase of co-volume also a function of the temperature, the increase of co-volume may be expressed as a function of the pressure.

Thus if V_p and V_o are the volumes of liquid at "p" and zero pressure:

$$V_p = V_o[1 + \phi(p)].$$

$\phi(p)V_o$ being therefore the co-volume at "p."

For another liquid, also expanding between "o" and "p":

$$V_p' = V_o'[1 + \phi'(p)].$$

At a higher pressure, p_1, the volumes become $V_o[1 + \phi(p_1)]$ and $V_o'[1 + \phi'(p_1)]$ respectively.

But as shown above, in the case of normal liquids:

$$\frac{V_o[1 + \phi(p_1)]}{V_o[1 + \phi(p)]} = \frac{V_o'[1 + \phi'(p_1)]}{V_o'[1 + \phi'(p)]};$$

that is

$$\frac{V_o'[1 + \phi(p_1)]}{V_o[1 + \phi(p_1)]} = \frac{V_o'[1 + \phi'(p)]}{V_o[1 + \phi(p)]}.$$

Therefore $\phi(p) = \phi'(p)$ and $\phi = \phi'$.

(1) The increase of co-volume is the same function of "p" for all these liquids. Assuming that the same law of expansion holds down to the lowest, and eventually, zero pressure:

$$\frac{V_o'[1 + \phi'(p)]}{V_o[1 + \phi(p)]} = \frac{V_{o'}}{V_{o'}}$$

(2) The co-volumes $V_{o'}\phi(p)$ and $V_o\phi(p)$ at any pressure are proportional to the actual volumes of the molecules $V_{o'}$ and V_o.

(3) The ratios between the volumes of the liquids at equal vapour pressures are equal to the ratios between the actual volumes of the molecules.

As soon as the vapour becomes so dense that the specific molecular attraction begins to have an effect in that phase, the nature of the relation between increments of vapour pressure and volume will probably change, and $\phi(p)$ take another form. By taking this into account, Mills (*J. Physical Chem.*, 1902, **6**, 209; 1904, **8**, 383, 593) has deduced the formula $\dfrac{q}{\sqrt[3]{d} - \sqrt[3]{D}}$ = constant for a series of normal liquids at different temperatures (q = inner heat of vaporisation of 1 gram liquid; d and D = densities of liquid and vapour). This equation holds up to the critical temperature. It can be shown that at temperatures so low that $\sqrt{D}$ may be left out of account compared with $\sqrt[3]{d}$ (considerably below the boiling point under atmospheric pressure), Mills' equation necessarily leads to the regularity mentioned above. For consider two liquids, A and B, at two pressures, P and P, and let Q be the total molecular latent heat of vaporisation and R the gas constant. To the values of P, T, Q and d for the two liquids assign the symbols:

$$\begin{array}{ccccccc} P' & T'_A & T'_B & Q'_A & Q'_B & d'_A & d'_B \\ P & T_A & T_B & Q_A & Q_B & d_A & d_B. \end{array}$$

Then for each liquid, by Mills' formula:

$$\frac{Q-RT}{Q'-RT'}\cdot\frac{\sqrt[3]{d'}}{\sqrt[3]{d}}=1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

Multiply by T'/T:

$$\frac{Q/T-R}{Q'/T-R}\cdot\frac{\sqrt[3]{d'}}{\sqrt{d}}=\frac{T'}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

Divide equation (2) for A by (2) for B:

$$\frac{Q_A/T_A-R}{Q_B/T_B-R}\times\frac{Q'_B/T'_B-R}{Q'_A/T'_A-R}\times\sqrt[3]{\frac{d'_A d_B}{d_A d'_B}}=\frac{T'_A.T_B}{T_A.T'_B}$$

But for normal liquids:

$$\frac{Q_A}{T_A}=\frac{Q_B}{T_B}, \text{ etc.}$$

Also
$$\frac{T'_A}{T'_B}=\frac{T_A}{T_B}+c\,(T'_A-T_A),$$

where "c" is very small, not greater than 0·0005 for the most dissimilar liquids: therefore

$$\sqrt[3]{\frac{d'_A}{d_A}}=\sqrt[3]{\frac{d'_B}{d_B}} \qquad \frac{d'_A}{d_A}=\frac{d'_B}{d_B}.$$

This relation can only be deduced from Mills' formula at temperatures at which the density of the vapour may be neglected. A recalculation of the constant (Mills, *J. Physical Chem.*, 1909, **13**, 512) has proved that the formula holds with the greatest accuracy in this region.

The assumption, then, that $\phi(p)$ remains constant down to the lowest pressure is in accordance with the above theory of molecular attraction, and with the facts of expansion down to the lowest vapour pressure at which liquid volumes have been compared.

The volumes at zero pressure could be found by extrapolation if the pressures were known with sufficient accuracy. The laws of expansion of liquids lead to an ideal state of zero co-volume for a perfect liquid, just as the laws of expansion of gases lead to the state of an ideal gas at the absolute zero.

In the case of liquids, however, it does not seem probable that the zero of pressure should occur at the same temperature in each case. The necessity for a special zero in each case has already been felt in explaining the deviations from the reduced equation of condition (Young, *Stoichiometry*, p. 237).

If it were possible, then, to obtain the liquid volumes of non-associated elements and compare them with the volumes of liquid non-associated compounds all at the same pressure, the ratios of these volumes would correspond with the ratios of the actual volumes of the molecules, the expansion or contraction on combination being thus discoverable.

Owing, however, to the scarcity of data, a direct comparison of this sort is in few cases possible, and where it can be made, most of the expansions are found to be not quite normal. The degree to which these irregularities influence the ratios will appear from the experimental data.

EXPERIMENTAL.

Materials.—The mercuric chloride was re-sublimed in a current of dry chlorine. Several analyses were made both of the freshly prepared salt and that which had been boiled for some time in the air, or heated in the dilatometer. The mercury was determined as mercuric sulphide, and the chlorine as silver chloride, and the results were satisfactory.

The mercuric bromide prepared to order by Hopkin and Williams gave satisfactory results on analysis, and was employed without further treatment in some cases. A sample redistilled with a little bromine gave identical results on analysis and in the dilatometer.

The mercuric iodide was also Hopkin and Williams' preparation. It was analysed by electrodeposition on a silver-plated platinum basin cathode, and gave theoretical results. It was afterwards redistilled to remove traces of a non-volatile impurity, which apparently did not affect the analysis, but made the liquid surface difficult to locate in the dilatometer.

Dilatometers.—These were of fused silica, and were supplied by the Silica Syndicate. They were graduated as required by a diamond fixed in place of the needle on a divider, and calibrated with mercury in the usual way. The bulbs were cylindrical, of about 2 c.c. capacity. The stems were graduated in mm., and each cm. length held from 0·02 to 0·03 c.c.

Thermometers.—Three nitrogen-filled mercury thermometers were used:

(1) Reading up to 600° in 2°; standardised at the National Physical Laboratory.

(2) To 600° in 2°, and (3) to 500° in 1°; these were standardised by comparison with (1).

Thermostats.—For temperatures up to 260° a bath of paraffin wax was used, and for these as well as higher temperatures the vapours of liquids boiling under various pressures were employed. These have been tabulated by Landolt and Börnstein from the measurements of Ramsay and Young as follows:

260—280°	Monobromonaphthalene.
280—302°	Diphenylamine.
360°	Mercury.

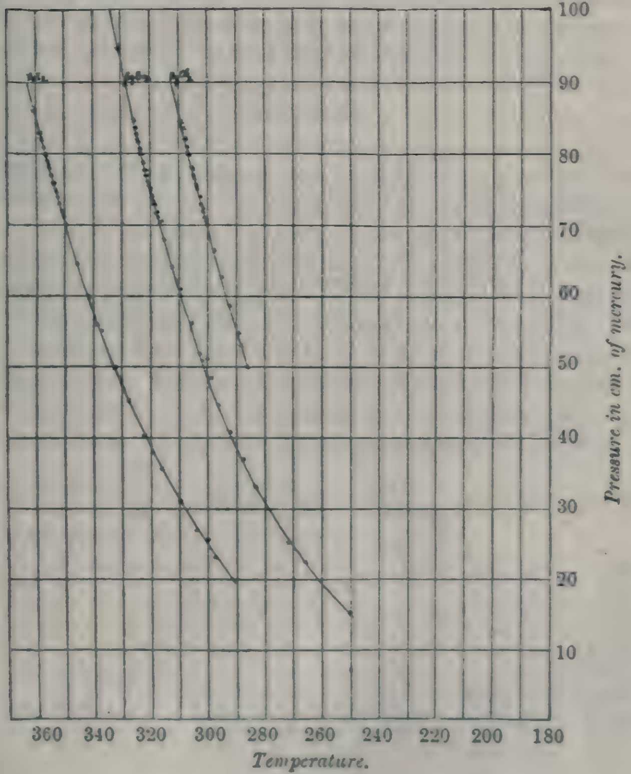
For the interval 310—339°, anthracene, boiling under diminished pressure, was used instead of the vapour of mercury.

The paraffin wax thermostat consisted of a large beaker of resistance glass jacketed with asbestos and heated by a gas flame from below. Additional heat was supplied by an electrically heated frame of iron wire in the liquid, which was stirred by a brass fan wheel at the bottom, and automatically regulated by a glass cylinder holding about 150 c.c. of air, which extended to the bottom of the liquid, and communicated by means of a capillary tube with a mercury gas regulator. The temperature could by this means easily be kept constant to a few tenths of a degree. The thermometers, etc., were not directly in contact with the liquid, but were protected by tubes of combustion glass.

The vapour-bath first used had somewhat the form of a Liebig's condenser. To a vertical glass tube open at each end was sealed an outer tube above and below. The vapour of the boiling liquid filled the space between the tubes. The liquid was contained in two side-bulbs joined to the lower end of the outer tube at an angle of about 45°. It was heated by burners and also electrically by platinum spirals. The electrical heating was used mainly to prevent bumping at low pressures. The lower part of the apparatus was protected by an asbestos box packed with magnesia. In order to save time, this was electrically heated by nickel wire. The upper part was shielded by movable rings of asbestos covered with felt. It was found that this form had several disadvantages when used for high boiling liquids—the radiation is large compared to the evaporating surface, and the dead space between the internal seal and junction of side-tubes adds considerably to the time required to send the ring of condensing vapour a sufficient distance up the tube. For the purpose in hand, however, the apparatus had the great advantage of allowing the introduction of dilatometers from below, so that they could be heated from the top downwards, thus avoiding the sometimes troublesome distillation of drops of liquid to the upper part of the tube.

In the form of vapour-bath afterwards used, the dilatometer was introduced from above into a glass tube about 2 cm. in diameter, which was heated by the vapour of a liquid boiling in a much larger bulb, the lower end of the inner tube being protected from the radiation of the superheated liquid by the well-known method recommended for thermometers in Young's *Fractional Distillation*. The vapour space was connected through a reservoir of about 10 litres capacity and a drying tower to a water exhaust pump or pressure pump as the case might be. The pressures were read on a mercury manometer attached to a wooden metre scale.

Vapour pressures of mercuric chloride, bromide, and iodide.



Vapour Pressures.—These were regulated and read by means of the air reservoir and mercury manometer already mentioned. The liquids were boiled under various pressures in a combustion glass tube. The sides of the tube were protected from overheating by horizontal pieces of asbestos board, and from cooling radiation by slip rings of asbestos covered with felt. The liquid was in every case boiled at such a rate that the thermometer column was completely immersed in the vapour. The bulb of the thermometer was covered with asbestos.

The results are tabulated below, and also shown in the figure.

The experimental points are indicated by X. A few vapour pressures at lower temperatures by Wiedemann, Stelzner, and Niederschulte (*Ber. deut. physikal. Ges.*, 1905, **7**, 159) are indicated as follows: mercuric chloride by circles, mercuric bromide by crosses, and mercuric iodide by circles. Most of these were deduced from the loss in weight when a measured quantity of air was passed over the solid at the temperature in question, and some by observing the pressure and temperature when the compounds were suddenly sublimed into a cooled tube. The curve so obtained ought not, of course, to be continuous with that of the vapour pressures of the liquids, but the observations in the neighbourhood of the melting point are not numerous enough for any discontinuity to be observed. The three observations recorded (by the authors quoted above) at higher temperatures do not agree with the present results, probably because the method they employed was not so suitable for higher temperatures. The pressures used for the subsequent calculations are those read from the manometer at 16·0°.

The following are the vapour pressures (to the nearest millimetre) corresponding with the corrected temperatures. The index numbers to the right of the pressures refer to different series of experiments.

Mercuric Chloride.

P. (mm.)	t°.	P.	t°.
844_2	309·0	751_3	303·0
836_1	308·2	741_2	302·5
822_2	307·5	730_3	302·7
820_3	308·1	724_2	301·5
816_1	306·8	719_3	301·9
810_3	307·5	711_3	301·4
803_2	306·7	705_2	300·5
800_3	307·0	702_3	300·8
798_1	305·9	690_4	300·0
790_3	306·4	665_2	297·5
781_2	305·1	627_2	294·8
780_3	305·8	612_4	294·5
778_1	304·9	587_2	292·0
770_3	305·0	582_4	292·3
766_3	304·8	548_2	289·0
759_4	304·3	544_4	289·4
757_2	303·9	530_2	287·9
754_1	303·6	505_4	286·1

Mercuric Bromide.

P. (mm.)	t°.	P.	t°
947_3	331·0	729_4	318·3
897_3	328·4	728_1	317·8
847_3	325·4	719_1	317·3
836_5	324·9	719_4	317·8
819_5	323·9	712_5	317·2
819_4	324·0	705_1	315·8
807_5	323·3	705_1	315·8
800_4	322·8	702_5	316·6
789_1	321·8	692_5	315·9
788_4	322·1	680_4	315·0
779_1	321·3	641_4	312·2
778_4	321·4	609_1	309·2
772_1	320·9	602_4	309·5
770_4	320·9	562_4	306·3
766_3	320·7	519_4	302·5
760_4	320·3	485_4	298·5
758_1	319·8	447_4	296·0
755_4	320·0	410_2	290·7
753_5	319·8	409_4	292·0
750_1	319·5	370_4	287·5
749_4	319·0	331_4	283·0
740_4	319·0	252_4	271·5
738_1	318·[illegible]	225_2	266·0

Mercuric Iodide.

P. (mm.)	t°.	P.	t°.
861_2	360·5	730_3	351·6
829_3	358·3	720_3	350·8
821_2	358·0	720_1	350·5
819_3	357·9	711_3	350·1
809_3	357·1	703_1	349·5
801_2	356·8	701_3	349·3
799_3	356·4	699_2	349·3
790_3	355·9	646_1	345·2
783_2	355·3	598_1	341·3
780_3	355·1	551_1	337·0
770_3	354·5	500_1	332·0
760_3	353·7	453_1	327·5
760_1	353·5	404_1	321·9
758_2	353·5	357_1	316·0
750_3	353·0	310_1	309·5
746_1	352·5	270_1	303·7
743_2	352·5	232_2	297·5
740_3	352·2		

A calculation of the value of heat of vaporisation divided by absolute temperature from the above data was undertaken, since this constant might be expected to throw some light on the question as to how far these compounds partake of the nature of fused salts. The values of Q/T for fused salts ought to be unusually high in view of the high degree of association which is usually attributed to them on other grounds (Bottomley, Trans., 1903, **83**, 1421; Lorenz and Kaufler, *Ber.*, 1908, **41**, 3727). The vapour-pressure curve was first investigated by Ramsay and Young's method. The absolute temperatures at which the compounds attain certain vapour pressures are tabulated below, and compared with the corresponding temperature for a standard liquid (fluorobenzene):

TABLE I.

	I.	II.	III.	IV.	I./IV.	II./IV.	III./IV.
P.	(THgCl$_2$).	T(HgBr$_2$).	T(HgI$_2$).	TC$_6$H$_5$F.			
240		542·0	572·0	325·5		1·665	1·757
300		551·5	581·5	331·5		1·664	1·755
530	561·0	576·5	608·5	347·0	1·617	1·662	1·754
700	573·0	589·0	622·5	356·0	1·610	1·655	1·749
800	579·5	596·0	629·5	360·5	1·608	1·653	1·747
860	583·0	599·5	633·5	363·0	1·606	1·651	1·746
900		601·5	636·0	364·0		1·650	1·745

From the above results a value of the constant was obtained in the equation:

$$\frac{T_A}{T''_B} = \frac{T_A}{T'_B} + c(T_B - T_B),$$

in which T_A are the temperatures of mercury halides, and T_B those of fluorobenzene at the same pressures.

"c" for $HgCl_2$ = 0·00050.
" " $HgBr_2$ = 0·00037.
" " HgI_2 = 0·00025.

The values of dP/dT were then found by a graphical method at a series of temperatures as tabulated below, and from these the heat of vaporisation Q and Q/T from the formula:

$$Q = \frac{1{\cdot}985\,T}{760}\left(T\frac{dP}{dT}\right) \text{ calories.}$$

Q and Q/T at 760 mm.

	Q(cal.)	Q/T
$HgCl_2$	13910	24·1
$HgBr_2$	14200	23·8
HgI_2	14700	23·5

It has been shown by Nernst that the normal value of Q/T at

760 mm. increases slightly with the boiling point of the liquid in question according to the formula:

$$Q/T = 9{\cdot}5\log.T - 0{\cdot}007T,$$

and for a liquid boiling at 304—354°:

$$Q/T = 22{\cdot}19 \text{ normally.}$$

There appears, then, to be a certain amount of association, less, however, than in the case of water and alcohols, for which $Q/T = 26$.

The association evidently diminishes in the order:

$$HgCl_2 \longrightarrow HgBr_2 \longrightarrow HgI_2.$$

Specific Gravities of the Liquids.

Procedure.—After the right weight (10—15 grams) had been introduced into the dilatometer, this was evacuated, sealed, and after a preliminary heating (great care is necessary to avoid bursting the dilatometer) introduced into one of the thermostats and kept at each temperature until the volume remained constant.

After the experiments were completed, the dilatometers were opened and the contents boiled out, the weight of substance being thus checked. In calculating the volumes corresponding with each scale division of the dilatometers, the expansion of the silica was not taken into account, since it proved to be outside the range of accuracy aimed at.

Thus the greatest range of temperatures was from 255° to 357°. The linear expansion of silica is:

$$0{\cdot}449 \times 10^{-6} \text{ or } 0{\cdot}59 \times 10^{-6}.$$

Taking the larger figure, $3\alpha = 1{\cdot}8 \times 10^{-6}$, and the total expansion of unit volume contained by a silica bulb at room temperature is $4{\cdot}59 \times 10^{-4}$ at 255°, and $6{\cdot}43 \times 10^{-9}$ at 357°.

The measured volumes have therefore to be increased, and the specific gravities decreased by about 1 in 2000.

This small correction has no effect on the relative specific volumes, but has been introduced into the absolute molecular volumes. The following specific gravities are calculated directly from the experimental data, the numbers to the left referring to different series of experiments in different thermostats with different quantities of compound and different thermometers.

Mercuric Chloride.

	t°.	D.		t°.	D.		t°.	D.
(1)	281·0	4·398	(3)	290·7	4·377	(5)	311·0	4·332
(2)	287·7	4·376		301·6	4·357		318·0	4·316
	290·7	4·369		304·6	4·348		328·0	4·293
	300·6	4·348	(4)	291·0	4·377		336·0	4·276
				301·5	4·357	(6)	357·0	4·238

Mercuric Bromide.

	t°.	D.		t°.	D.		t°.	D.
(1)	240·0	5·112	(3)	253·0	5·066	(4)	302·0	4·908
	244·0	5·110		258·0	5·052	(5)	258·5	5·054
	251·0	5·078		260·0	5·044		280·5	4·976
	261·5	5·046	(4)	254·5	5·062		292·0	4·944
(2)	241·5	5·104		260·0	5·044		301·5	5·054
	248·0	5·082		272·0	5·007	(6)	313·0	4·874
	252·0	5·071		278·0	4·990		320·0	4·844
	259·0	5·048		286·5	4·964		329·5	4·811
(3)	250·0	5·076		293·5	4·938		339·0	4·784

Mercuric Iodide.

	t°.	D.		t°.	D.		t°.	D.
(1)	254·5	5·236	(2)	281·0	5·160	(4)	294·5	5·119
	260·5	5·218	(3)	275·0	5·177		301·5	5·090
	266·0	5·207		279·0	5·166	(5)	311·5	5·075
	270·0	5·190		283·0	5·154		323·0	5·039
	276·0	5·169		286·0	5·141		329·5	5·014
	281·0	5·157		292·0	5·125		337·5	4·985
(2)	259·5	5·226		294·5	5·113		339·0	4·978
	267·5	5·208		301·5	5·090	(6)	339·0	4·967
	275·0	5·177	(4)	282·5	5·154	(7)	356·0	4·915

The alteration of density with temperature can be expressed as follows:

Mercuric Chloride, 280—335°:

$$D_t = 4{\cdot}400 - 0{\cdot}002218\ (t^\circ - 280).$$

Mercuric Bromide, 240—340°:

$$D_t = 5{\cdot}116 - 0{\cdot}00338\ (t^\circ - 240).$$

Mercuric Iodide, 255—355°:

$$D_t = 5{\cdot}238 - 0{\cdot}00322\ (t^\circ - 255).$$

Densities and Vapour Pressures of the Elements Compared with those of Compounds.

The data taken from the tables require no comment.

The densities of liquid iodine are those of Billet from *Constants of Nature* (Smithsonian). They appear somewhat irregular, which is due probably to the dark colour of the vapour at the higher temperatures. Special weight has been given to the values at the lower temperatures, and that found at the boiling point by Drugman and Ramsay (Trans., 1900, **77**, 1228). The column headed "pressure" refers as throughout to that of the saturated vapour:

TABLE II.

Density.

Pressure.	Cl_2.	Br_2.	I_2.	Hg.	$HgCl_2$.	$HgBr_2$	HgI_2.
200	1·617	3·109	3·888	12·901		5·037	5·124
400	1·585	3·050	3·795	12·824		4·944	5·026
560	1·572	3·018	3·749	12·785	4·380	4·890	4·970
760	1·558	2·985	3·705	12·747	4·348	4·840	4·920
860	1·550	2·975	3·685	12·738	4·336	4·821	4·900

The expansions over certain intervals of pressure are compared with the normal below. Since the volumes are accurate to 0·2 per cent., the expansion, for example, between 560 and 860 mm. of mercury is 0·010 ± 0·002 in the case of mercuric chloride, and this is distinctly below the normal value. Thus for the pressure interval named, the value of the ratio $D(560)/D(860)$ is: Normal 1·023, Hg 1·003, Cl_2 1·014, Br_2 1·014, I_2 1·017, $HgCl_2$ 1·010, $HgBr_2$ 1·014, HgI_2 1·014.

The cause of these abnormalities is probably association as affecting not so much the liquid volumes as the vapour pressures, and hence the temperatures of comparison [see van't Hoff, *Lectures*, III, p. 27 (Lehfeldt)].

From the numerical values of the expansion the degree of association would appear to diminish in the order:

$$Cl_2 \longrightarrow Br_2 \longrightarrow I_2;\ HgCl_2 \longrightarrow HgBr_2 \longrightarrow HgI_2.$$

Now, comparing the expansions of the compounds with those of their constituent elements, it may be seen that the magnitude of the abnormality is such as would be produced if the expansion were additively composed of the expansions of the elements.

Thus the ratios		$\frac{V_M(860)}{V_M(560)}$	and	$\frac{\Sigma V_A(860)}{\Sigma V_A(560)}$
are, for	$HgCl_2$ and Hg + 2Cl	1·010	and	1·012
	$HgBr_2$,, Hg + 2Br	1·014	,,	1·012
	HgI_2 ,, Hg + 2I	1·014	,,	1·015

While the magnitude of the possible volume error (14—20 per cent. on the expansion) does not permit of a certain conclusion on this point, yet the evidence for such a relation is strengthened by an examination of the few other compounds for which data are available.

Thus, comparing the ratios V_M and ΣV_A at 760 and 200 mm.:

PCl_3	1·050	P + 3Cl	1·050
ICl	1·041	I + Cl	1·043

The importance of this for the question in hand rests in the increased constancy it gives to the ratio $V_M/\Sigma V$ under various pressures.

In the first part of the paper reasons were given why the ratio should be quite constant in the case of normal elements and compounds far enough removed from their critical points.

It now appears that a constant ratio $V_M/\Sigma V_A$ can also be defined for the abnormally expanding elements and compounds considered, as may be seen from table III.

The variations of the ratios are within the limits of error to be expected from at least one of the volume measurements involved.

TABLE III.

100 *Volumes of the Elements become on Combination*

	P=860 mm.	760	560	
$HgCl_2$,Hg+2Cl	101·9	101·8	101·7	—
$HgBr_2$	107·5	107·4	107·3	—
HgI_2	109·5	109·5	109·6	—
	P=760 mm.	560	400	200
$PCl_3 \longrightarrow P+3Cl$	105·6	105·2	104·9	105·0
PBr_3	107·8	—	—	107·5
PCl_5	96·5	—	—	—
PBr_5	101·9	—	—	101·6

NOTE.—The vapour pressures and atomic volumes of the phosphorus halides and iodine chloride (referred to on p. 2042) are taken from the tables and Trans., 1907, **91**, 1711; 1909, **95**, 445. The temperature corresponding with 200 mm. for phosphorus tribromide has been calculated by Ramsay and Young's method (comparison liquid, phosphorus trichloride).

The expansion on combination therefore increases with increasing atomic weight for the mercuric halides as for the other compounds quoted (except phosphorus pentachloride, in which case the contraction on combination diminishes). According to the first part of this paper, the changes of volume on combination are approximately equal to the difference between the sums of the interatomic volumes of elementary molecules and the interatomic volume of the compound molecule. If this is correct the physical interpretation to be put upon the results is that, for example, the interatomic volume of a Cl_2 molecule is less than that of $HgCl_2$ (Hg being monatomic), and that in the other cases (except PCl_5) the sums of the interatomic volumes of the elementary molecules are less than the interatomic volume of the compound molecule. Now, comparing together two similar combinations, such as mercuric chloride and bromide, the relative increase of interatomic volume on combination is greater in the latter case, indicating a smaller molecular attraction for the atoms of mercuric bromide than for those of mercuric chloride. In the case of phosphorus halides, also, the bromide combination exhibits a smaller molecular attraction as judged by these volume relations than the chloride. Thus the relative affinities are in the few cases investigated in the same order as the same affinities deduced from other considerations.

I desire to express my thanks to the Royal Society for a grant in aid of this research, and to Professor Donnan for the facilities afforded at the Muspratt Laboratory and the interest he has taken in the work.

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CCXIV.—*Contributions to our Knowledge of the Sulphide Dyestuffs. Part I.*

By GEORGE HERBERT FRANK.

SINCE the introduction of Vidal black (by R. Vidal, of Paris, in 1893), which, as is well known, is prepared by fusing together *p*-aminophenol (or *p*-aminophenol and other compounds) with sodium polysulphide, a large number of these so-called "sulphide" dyestuffs have been produced in a similar manner from aromatic compounds of varied constitution. The application of these colouring matters, especially to cotton, is of so simple a character, and the colours obtained are of so permanent a nature, that these compounds now constitute one of the most important groups of artificial dyestuffs. Although considerable insight has been gained as to the reactions occurring in their formation (Vidal, *Mon. Sci.*, 1903, [iv], **17**, i, 427; Pollak, *Zeitsch. Farb. Ind.*, 1904, **3**, 233, 253; Gnehm and Kaufler, *Ber.*, 1904, **37**, 2617, 3032), the subject is beset by considerable difficulty, for the dyestuffs are as a rule amorphous, of a comparatively insoluble nature, do not yield well-characterised derivatives, and are accordingly not easily isolated in a pure condition.

During some experiments on the subject it was discovered that the leuco-compounds of many sulphide dyestuffs react with chloroacetic acid, and that the substances thus obtained, when oxidised, yield interesting colouring matters, differing considerably in properties from the parent substance. These new carboxyl derivatives are readily soluble in alkalis, pyridine or phenol, moderately so in boiling alcohol or acetic acid, but insoluble in dilute acids. They are well-defined colouring matters, giving shades similar to those produced by the original sulphide dyes, and can be readily dyed on wool, but differ from the parent sulphide dyes in that they have very little affinity for cotton.

Among other points of interest attached to these substances it seemed possible that their closer examination would yield an insight as to the true molecular weight of the sulphide dyestuffs from which they were obtained, a point which would be of considerable help in regard to the vexed question of their constitution.

The following investigation deals with the well-known colouring matter, immedial-indone, which is manufactured by heating together *p*-aminophenol and *o*-toluidine with an aqueous solution of sodium sulphide. In order to purify the commercial product, it was repeatedly washed with warm water, treated with dilute hydrochloric acid until the liquor was faintly acid, and well washed. Fifty grams of the finely powdered product were reduced with sodium hydroxide and dextrose at 60—70° in the usual manner, and treated with 20 grams of a solution of sodium chloroacetate. An increase in temperature took place, and after fifteen minutes air was aspirated through the liquid in order to oxidise the leuco-compound. The liquid was now neutralised with dilute hydrochloric acid, the precipitated dye collected, extracted with warm sodium carbonate solution, the extract acidified, and the dye collected and dried; the product was now extracted with warm aniline, filtered from a slight residue, the solution neutralised with acid, and the precipitate again extracted with dilute sodium carbonate solution and acidified. As molecular-weight determinations in pyridine and nitrogen and sulphur estimations indicated that this product was not quite pure, it was submitted to a further treatment with warm aniline and extraction with dilute aqueous sodium carbonate in the manner above described, and finally dried in a vacuum desiccator. The compound obtained in this way contained no ash, and experiments indicated that it was now pure. It was of a deep blue, bronzy colour, readily soluble to a blue solution in aniline, pyridine, phenol, alkalis, or concentrated sulphuric acid, and sparingly so in hot glacial acetic acid or hot alcohol. Experiment indicated the absence of an amino-group, and, unlike the original immedial-indone, it had no affinity for cotton when dyed in a sodium sulphide bath, neither had its sodium salt any affinity for cotton, but the latter could be dyed on wool in the manner of an acid colour, giving a bright blue colour.

After being dried at 98°, it was analysed:

0·1241 gave 0·2494 CO_2 and 0·0459 H_2O. C = 54·8; H = 4·11.
0·2800 „ 17·3 c.c. N_2 at 13° and 757·7 mm. N = 7·40.
0·1121 „ 0·1376 $BaSO_4$. S = 16·88.

0·1312 gave 0·1559 $BaSO_4$. S = 16·72.

$C_{17}H_{14}O_4N_2S_2$ requires C = 54·4; H = 4·0; S = 17·07; N = 7·48 per cent.

0·5 Gram of the substance was treated with 10 c.c. of *N*-sodium hydroxide, and the solution was made up to 500 c.c.; by titration with *N*/10-hydrochloric acid and employing phenolphthalein as indicator, the acidity of the compound was first determined, and the neutral liquid thus produced was then treated with sodium tartrate and reduced with standard titanium chloride:

Found, NaOH = 21·12 per cent. of the weight of the dye.
" H_2 = 0·529 " " " "
$C_{17}H_{14}O_4N_2S_2$ requires NaOH = 21·39; H_2 = 0·5347 per cent.

Hence 189·9 parts of the colouring matter neutralise 40 parts of sodium hydroxide, and for the reduction of 378·2 parts, 2 parts of hydrogen are required.

A determination of the molecular weight was carried out by the cryoscopic method:

0·0854, in 10·3 of phenol, gave $\Delta t = -0·14°$. M.W. = 377·4.

$C_{17}H_{14}O_4N_2S_2$ requires M.W. = 374.

When fused with sodium hydroxide, the substance undergoes an interesting change, for not only is sulphur thus removed, but also the carboxyl groups are eliminated. A blue compound insoluble in water or alkalis is thus produced. When reduced, this yields a leuco-derivative, but, unlike the corresponding leuco-derivatives of the sulphide dyestuffs, possesses no affinity for cotton.

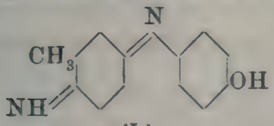
To obtain some further indication as to the nature of the reaction, a quantitative experiment was carried out as follows:

0·5 Gram of the carboxyl derivative was fused at 200° with concentrated aqueous sodium hydrate until a colourless pasty mass, consisting of the leuco-compound of the new substance, was produced. The product when cold was diluted with water, the mixture neutralised with acid, and the colouring matter collected and washed. An estimation of the sulphur present gave the following result:

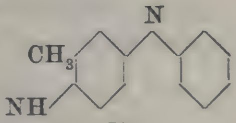
0·154 gave 0·1668 $BaSO_4$. S = 14·89 per cent.

Hence 215 parts of the substance contain 32 parts of sulphur. If from the found molecular weight of the carboxyl derivative we subtract $2(CH_2{\cdot}CO_2H) + S = 150$, the new substance should have a molecular weight of 227, which is in fair agreement with the above result. This experiment shows that one atom of sulphur can be removed from the molecule of the original carboxyl derivative, but that, on the other hand, the removal does not destroy the chromophoric group of this compound.

As immedial-indone is formed from the indophenol (I) obtained from *p*-aminophenol and *o*-toluidine, so the resultant dyestuff may be expected to possess the skeleton (II):

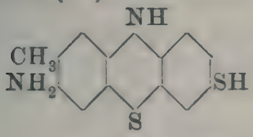


(I.)

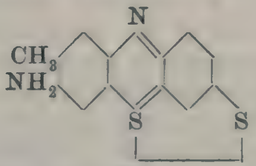


(II.)

If we assume that, as is most probable during the reaction, sulphur enters in the *o*-position with respect to the nitrogen atom, and that the phenolic group is replaced by the thiol group, leuco-immedial-indone would have the constitution (III), and immedial-indone formula (IV):

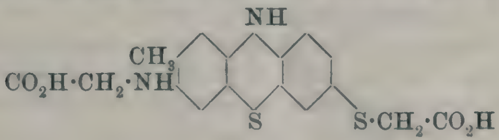


(III.)

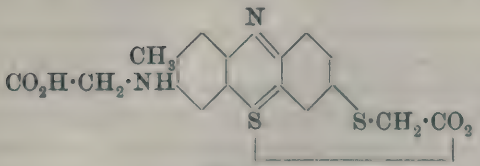


(IV.)

Such a constitution would offer a ready explanation of the experiments given above. This compound would readily yield with chloroacetic acid a leuco-dicarboxylic derivative having the formula (V), and the colouring matter would be represented by (VI).



(V.)



(VI.)

This investigation therefore indicates that the most probable constitution of immedial-indone is that given above; further experiments on this difficult subject are in progress.

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CCXV.—*The Reactivity of Ketones towards Iodine and the Relative Rates of Tautomeric Change.*

By HARRY MEDFORTH DAWSON and ROBERT WHEATLEY, B.Sc.

IN a previous paper (Dawson and Leslie, Trans., 1909, **95**, 1860) it has been shown that iodine reacts readily with acetone at the ordinary temperature, and that when aqueous solutions containing acetone and iodine are acidified by addition of a mineral acid, the reaction proceeds at a rate which is suitable for accurate quantitative measurements. These observations showed that when the acetone is present in considerable excess, the rate of disappearance of the iodine is practically constant from the commencement until near the end of the reaction, the velocity being proportional to the concentration of the acetone and of the added mineral acid.

To account for these facts, the view was adopted that the reaction between acetone and iodine involves two stages. In the first of these, the acetone is converted from the ketone into the enolic form, and this is then acted on by the iodine at a relatively very rapid rate with the formation of iodoacetone. In consequence of the very great difference in the velocities of the consecutive reactions, the rate of disappearance of the iodine is determined solely by the rate at which the acetone is transformed into the enolic form (compare Lapworth, Trans., 1904, **85**, 30).

If this is the correct interpretation of the facts, it is evident that the investigation of the velocity of reaction of iodine with other ketones should lead to information respecting the rates at which the various ketones undergo tautomeric change. With this object in view, experiments were made to compare the rates of disappearance of iodine in dilute acidified solutions of dimethyl, methyl ethyl, methyl propyl, methyl butyl, methyl hexyl, phenyl methyl, diethyl, and phenyl ethyl ketones. On account of the small solubility of certain of these ketones in water, the comparative measurements could not be made in aqueous solution, and instead of this, an aqueous alcoholic solution containing forty volumes per cent. of ethyl alcohol was employed. In this connexion experiments were made to ascertain the influence of the medium on the reaction between acetone and iodine in alcohol–water mixtures ranging from pure water to pure alcohol. The results of this investigation will be communicated in a further paper. For the present it is sufficient to state that the reaction between the two substances is of the same character in alcoholic as in aqueous solution, and that, for a given concentration of acetone and acid, the rate of disappearance of iodine is practically the same in alcohol–water mixtures as it is in pure water, if the amount of alcohol present does not exceed sixty to seventy volumes per cent. The only difference to be noted is the displacement of the final equilibrium as the ratio of the two components in the solvent is gradually altered. This influence of the medium is shown by the data in table I, which were obtained in parallel experiments with solutions containing 0, 20, 40, 60, 80, and 100 volumes per cent. of alcohol. The temperature at which these measurements were made was 25·1°.

TABLE I.

Initial iodine concentration = 0·0095; acetone = 0·272 *; H_2SO_4 = 0·1 mol. per litre.

Volumes per cent. alcohol	0	20	40	60	80	100
Equilibrium iodine concentration	0·000005	0·000015	0·00040	0·00100	0·00225	0·00442
Percentage of unchanged iodine	0·05	0·15	4·2	10·5	23·7	46·5

* This concentration corresponds with 20 c.c. of acetone per litre.

These results show that the limit of the reaction is reached at a progressively earlier stage as the proportion of alcohol in the solvent increases, and the range of the velocity measurements is correspondingly diminished. In presence of potassium iodide, the reaction takes place still less completely. In the case of the first three solutions in the above table, the percentage of unchanged iodine was found to be 0·8, 2·3, and 16·9 respectively when potassium iodide was present to the extent of 0·02 mol. per litre. This effect of the iodide is no doubt due to the removal of iodine in consequence of the formation of polyiodides. In choosing a 40 per cent. alcoholic solution as the medium for the reacting substances, these circumstances were taken into consideration, and the alcohol-water mixture in question represents the smallest proportion of alcohol which is necessary for the solution of the majority of the ketones in the requisite concentration.

The limit of the reaction in the aqueous-alcoholic solution varies with the nature of the ketone. This is evident from a consideration of the data in table II, which gives the results obtained for acetone, diethyl ketone, and acetophenone. In these and all other experiments the relative concentrations of ketone and iodine were such that the active mass of the ketone could be regarded as constant during the course of the reaction. Similarly, the concentration of the sulphuric acid was so large that no appreciable alteration in its value resulted from the formation of the hydriodic acid during the reaction.

The ketone was weighed out into a graduated stoppered flask containing water and measured quantities of alcohol and standard sulphuric acid solution. The flask was placed in a thermostat at 25·1°, and after some time a known quantity of iodine was added in the form of an aqueous potassium iodide solution, and the contents were made up to the mark with water. After definite time intervals, portions of the solutions were removed, added to excess of a sodium hydrogen carbonate solution, and titrated with a freshly prepared 0·01*N*-solution of sodium thiosulphate.

In the following tables x_1 is the observed iodine concentration in mols. per litre, and x_2 the concentration calculated from the equation $x_2 = x_0 - kt$, in which x_0 is the first observed concentration ($t=0$), and k the velocity constant $= dx/dt$. The concentrations of the ketone and the acid and the original concentration of the iodine are given in every case in mols. per litre.

TABLE II.

Acetone.

Acetone = 0·1886; H_2SO_4 = 0·1; iodine = 0·0101.

Time (minutes)	0	25	45	65	85	105	140	24 hours
$x_1 . 10^4$	91·8	77·8	67·4	57·2	46·9	37·9	27·5	20·3
$x_2 . 10^4$	(91·8)	78·3	67·5	56·7	45·9	35·1	16·2	—

$k = 0·000054$.

Diethyl Ketone.

Ketone = 0·2532; H_2SO_4 = 0·1; iodine = 0·0102.

Time (minutes)	0	30	60	80	105	120	135	24 hours
$x_1 . 10^4$	90·4	72·7	54·7	43·0	28·5	20·4	12·9	2·2
$x_2 . 10^4$	(90·4)	72·7	55·0	43·2	28·4	19·6	10·8	—

$k = 0·000059$.

Acetophenone.

Ketone = 0·1673; H_2SO_4 = 0·1; iodine = 0·0101.

Time (minutes)	0	15	51	75	105	135	165	255	24 hour
$x_1 . 10^4$	98·3	95·6	89·2	84·8	79·3	74·5	70·2	57·7	42·4
$x_2 . 10^4$	(98·3)	95·6	89·1	84·8	79·4	74·0	68·6	52·4	—

$k = 0·000018$.

From a comparison of the equilibrium iodine concentrations recorded under $t = 24$ hours, it is evident that the extent to which the reaction proceeds is dependent on the nature of the ketone in solution. Although the above three experiments are not strictly comparable because of the differences in the ketone concentrations, it is seen that in the acetone, diethyl ketone, and acetophenone solutions the unchanged iodine amounts to about 20, 2, and 40 per cent. respectively. Of the ketones examined, the reaction proceeds furthest in the case of diethyl ketone, and to the smallest extent in the case of acetophenone, and on this account data are recorded for these two substances, as well as for acetone, which show the progress of the reaction throughout the greater part of its course.

On comparing the values of x_1 and x_2, it is seen that in the case of acetone, the rate of disappearance of the iodine is constant until about 50 per cent. of the iodine originally present has reacted, and that the velocity then diminishes as the equilibrium condition is approached. For diethyl ketone the velocity remains constant until about 75 per cent. of the iodine has disappeared, whereas, in the case of acetophenone, the velocity shows distinct evidence of diminution when about 30 per cent. of the iodine has reacted. The point at which the velocity begins to fall is obviously determined by the proportion of the original iodine which remains when the condition of equilibrium has been reached. The more complete the reaction, the greater is the range over which the reaction velocity remains constant.

In the communication of further results this circumstance is taken into consideration, and the measured velocities relate solely to that part of the total reaction in which the iodine disappears at a constant rate. Table III contains the data obtained in experiments with other ketones, the calculated iodine concentrations being placed alongside the observed values, as in table II:

TABLE III.

Methyl Ethyl Ketone.

Ketone = 0·174; H_2SO_4 = 0·095 mol. per litre.

Time (minutes)	0	30¼	57½	85½	129
$x_1 . 10^4$	94·8	79·4	66·1	52·9	34·4
$x_2 . 10^4$	(94·8)	79·8	66·3	52·5	31·2

$k = 0·0000495$.

Methyl Propyl Ketone.

Ketone = 0·1727; H_2SO_4 = 0·1 mol. per litre.

Time (minutes)	0	30	47	60	95
$x_1 . 10^4$	92·1	78·0	69·8	64·0	47·6
$x_2 . 10^4$	(92·1)	78·0	70·0	63·9	47·5

$k = 0·0000453$.

Methyl Butyl Ketone.

Ketone = 0·1678; H_2SO_4 = 0·1 mol. per litre.

Time (minutes)	0	25	45	60	85
$x_1 . 10^4$	89·5	76·3	66·2	58·1	45·5
$x_2 . 10^4$	(89·5)	76·4	66·0	58·1	45·1

$k = 0·0000523$.

Methyl Hexyl Ketone.

Ketone = 0·0814; H_2SO_4 = 0·1 mol. per litre.

Time (minutes)	0	30	70	100	130
$x_1.10^4$	73·3	65·8	55·7	48·3	41·2
$x_2.10^4$	(73·3)	65·8	55·8	48·3	40·8

k = 0·000025.

Phenyl Ethyl Ketone.

Ketone = 0·0855; H_2SO_4 = 0·251 mol. per litre.

Time (minutes)	0	120	235	350	480	565
$x_1.10^4$	96·6	90·0	83·6	78·3	71·8	67·4
$x_2.10^4$	(96·6)	90·4	84·4	78·4	71·6	67·2

k = 0·0000052.

In addition to the above experiments others were made in which the concentrations of the various ketones and of the acid were approximately doubled or halved. These indicate that the various reactions take place at a rate which is proportional to the ketone and acid concentrations, as was found to be the case for the action between iodine and acetone in aqueous solution. Apart from the constancy of the reaction velocity, the fact that the influence of ketone and acid concentration is the same for all the ketones examined affords strong evidence in support of the view that the cause of the uniform speed of the reaction is the same in all cases, that is to say, a change in the ketone from the ketonic to the enolic form.

On the basis of the observed proportionality between the velocity and the ketone and acid concentrations, the several values obtained for the speed of the reactions may be reduced to a uniform ketone and acid concentration (ketone = 1/6 mol. per litre; sulphuric acid = 0·1 mol. per litre). In this way the velocities of reaction recorded in the second column of table IV are obtained. These numbers may be taken as representing the relative rates at which the ketonic forms of the various members of the series are converted into the corresponding enolic forms. The velocities with reference to acetone as standard are given in the third volume.

TABLE IV.

Ketone.	k (mols. per litre per minute).	Relative k values.
Acetone	48×10^{-6}	1
Methyl ethyl ketone	50×10^{-6}	1·04
Methyl propyl ketone	45×10^{-6}	0·94
Methyl butyl ketone	53×10^{-6}	1·10
Methyl hexyl ketone	51×10^{-6}	1·06
Acetophenone	18×10^{-6}	0·37
Diethyl ketone	$39{\cdot}5 \times 10^{-6}$	0·82
Phenyl ethyl ketone	$4{\cdot}0 \times 10^{-6}$	0·083

From the above values of k, it is seen that the replacement of one of the methyl groups in acetone by ethyl, propyl, butyl, or hexyl does not cause very much alteration in the rate at which the substance reacts with iodine. On the other hand, the reactivity is reduced to nearly one-third when the methyl group is replaced by phenyl. For diethyl ketone the velocity is only about 20 per cent. smaller than in the case of acetone, and substitution of phenyl for one of the ethyl groups reduces the reactivity to about one-tenth.

On the assumption that the measured velocities are determined by the respective rates of tautomeric change, it is not surprising that the first five ketones should be found to react with iodine at approximately the same rate, for in each case the transformation involved may be supposed to be that represented by

$$CH_3{\cdot}CO{\cdot}R \longrightarrow CH_2{:}C(OH){\cdot}R.$$

On the other hand, the fact that the reactivity of diethyl ketone is nearly as great as that of the methyl ketones would seem to show that the change represented by

$$CH_3{\cdot}CH_2{\cdot}CO{\cdot}R \longrightarrow CH_3{\cdot}CH{:}C(OH){\cdot}R$$

may take place almost as readily as the previous one. That this approximate equality of the rates of change of the groups $CH_3{\cdot}CO{\cdot}$ and $CH_3{\cdot}CH_2{\cdot}CO{\cdot}$ is not general, however, is evident from a comparison of the values for acetophenone and phenyl ethyl ketone. As shown by experiments with benzophenone, the phenyl group does not react at all with iodine under the conditions of the dynamic experiments, and it might be expected that the ratio of the reactivities of these two substances would be the same as the ratio found in the case of acetone and diethyl ketone. This is not the case, the observed velocity of reaction in the case of acetophenone being about four and a-half times as great as that found for phenyl ethyl ketone. In other words, the relative rates at which the groups $CH_3{\cdot}CO{\cdot}$ and $CH_3{\cdot}CH_2{\cdot}CO{\cdot}$ undergo tautomeric change is dependent on the nature of the radicle with which the two groups are combined. On the other hand, the approximate equality of the rates of reaction of dimethyl and diethyl ketone with iodine leads us to anticipate that methyl ethyl ketone will react with iodine in two ways, which are determined respectively by the tautomeric changes:

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_3 \longrightarrow CH_2{:}C(OH){\cdot}CH_2{\cdot}CH_3 \text{ and}$$
$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_3 \longrightarrow CH_3{\cdot}C(OH){:}CH{\cdot}CH_3.$$

The amounts of the corresponding iodo-substitution products will be conditioned by the relative rates at which these two changes take place. On the basis of the results which have been obtained with the aliphatic ketones, it appears probable that aliphatic ketones will in general give rise to two substitution products, for the velocities of the two possible tautomeric changes are apparently of the same order of magnitude.

Preliminary experiments have been made which show that certain aldehydes react with iodine in a similar manner to that observed for the various ketones investigated in this paper. This is the case for propaldehyde, whereas the kinetic investigation of the reaction between acetaldehyde and iodine indicates that the mechanism of this change is of a different kind. This question is being further investigated.

The chief results obtained in this inquiry are:

1. Evidence is adduced to show that the mechanism involved in the reaction of iodine on various ketones is of the same kind, the progress of the change being determined by the rate at which the enolic form of the ketone is formed.

2. From the measurement of the velocities with which the ketones react with iodine, the relative rates at which the ketones undergo tautomeric change have been obtained.

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LEEDS.

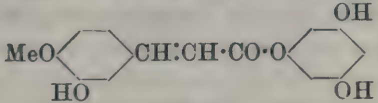
CCXVI.—*The Constitution of Eriodictyol, of Homoeriodictyol, and of Hesperitin.*

By FRANK TUTIN.

IN a paper communicated to the meeting of the American Pharmaceutical Association, held at Indianapolis, Ind., in September, 1906, Dr. F. B. Power and the present author described the isolation of two crystalline substances of phenolic nature from the leaves of *Eriodictyon Californicum* (Hooker and Arnott), Greene (*Proc. Amer. Pharm. Assoc.*, 1906, **54**, 352). These two compounds were designated eriodictyol and homoeriodictyol respectively, the former having been proved to possess the formula $C_{15}H_{12}O_6$, whilst the composition of the latter was shown to be $C_{16}H_{14}O_6$.

In a subsequent communication (Trans., 1907, **91**, 887) it was noted that there are certain similarities in the properties of homoeriodictyol and its isomeride, hesperitin, which suggested that these two compounds were structurally related. Experiments supported this view, for, whilst hesperitin yields *iso*ferulic acid (3-hydroxy-4-methoxycinnamic acid) and phloroglucinol on hydrolysis (Tiemann and Will, *Ber.*, 1881, **14**, 970), homoeriodictyol, when similarly treated, gave the same phenol together with ferulic acid (4-hydroxy-3-methoxycinnamic acid).

Tiemann and Will (*loc. cit.*) assigned to hesperitin the constitutional formula (I). This formula received support through the

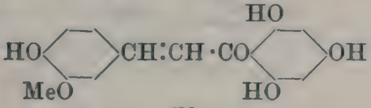


$\mathrm{MeO(HO)C_6H_3\cdot CH{:}CH\cdot CO\cdot O\cdot C_6H_3(OH)_2}$

(I.)

work of A. G. Perkin (Trans., 1898, **73**, 1037), who prepared acetylhesperitin, and recorded results which indicated that this compound was a triacetyl derivative.

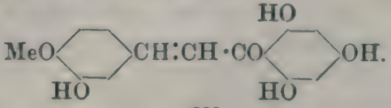
It appeared therefore from the results of the hydrolysis experiments mentioned above that homoeriodictyol differed from hesperitin only in the relative positions of the hydroxyl and methoxyl groups in the catechol part of the molecule. When, however, acetylhomoeriodictyol was prepared, it was found to contain four acetyl groups. It was therefore concluded that homoeriodictyol must be represented by formula (II).



$\mathrm{HO(MeO)C_6H_3\cdot CH{:}CH\cdot CO\cdot C_6H_2(OH)_3}$

(II.)

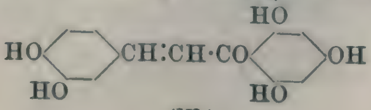
From this it would appear that homoeriodictyol was not so similar to hesperitin in structure as had at first been concluded. Nevertheless, Dr. Power and the present author were so convinced of the near relationship of these two compounds that they ventured to suggest that the formula hitherto assigned to hesperitin is incorrect, notwithstanding the statement of Perkin (*loc. cit.*) that the latter yields only a triacetyl derivative. Formula (III) was therefore put forward for hesperitin.



$\mathrm{MeO(HO)C_6H_3\cdot CH{:}CH\cdot CO\cdot C_6H_2(OH)_3.}$

(III.)

With regard to the constitution of eriodictyol, the amount of material which was at first available did not permit of many experiments being conducted with this substance, but the view was expressed that it was the parent compound of which hesperitin and homoeriodictyol are monomethyl ethers (formula IV).

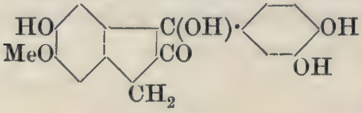


$\mathrm{(HO)_2C_6H_3\cdot CH{:}CH\cdot CO\cdot C_6H_2(OH)_3}$

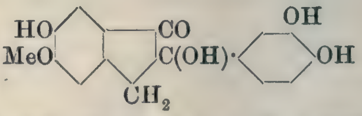
(IV.)

Shortly after the appearance of the first paper by Power and Tutin on eriodictyon leaves (*loc. cit.*), a communication on the same subject was published by G. Mossler (*Annalen*, 1907, **351**, 233). This author recorded the isolation of a substance possessing the formula $C_{16}H_{14}O_6$, designated "eriodictyonon," which was evidently identical with homoeriodictyol. Mossler, however, did not succeed in isolating any eriodictyol.

After having published the account of their work on the constitution of homoeriodictyol, Dr. Power and the present author received from Dr. Mossler a reprint of a paper communicated by him to the Academy of Sciences in Vienna (*Sitzungsber. K. Akad. Wiss. Wien*, 1907, **116**, ii, June, 1907). In this communication Mossler, who was unaware of the more recent work of the abovementioned authors, admits that his "eriodictyonon" is identical with homoeriodictyol, and sets forth the conclusion that this substance is represented by one of the following formulæ:



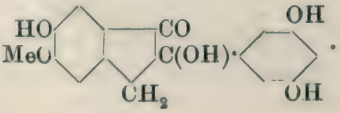
or



This last publication by Mossler was replied to by Dr. Power and the present author (Proc., 1907, **23**, 243), when it was pointed out that neither of the formulæ proposed by Mossler could be correct, since compounds possessing such a structure could not yield phloroglucinol.

One statement made by Mossler, however, was in direct conflict with the views which the present author, in conjunction with Dr. Power, had expressed regarding the constitution of homoeriodictyol, namely, that the substance in question was optically active. The last-mentioned authors were unable to confirm this, and, since the correctness of their conclusions regarding homoeriodictyol have now been fully proved, it is evident that the above statement of Mossler must have been based on an incorrect observation.

It appeared to the present author that there was one possible alternative to the formula which had been suggested by him in conjunction with Dr. Power for homoeriodictyol, but which was not at all probable, namely, a structure related to the second formula proposed by Mossler, as follows:



A substance possessing such a formula might conceivably yield, on hydrolysis, phloroglucinol and ferulic acid by the addition of two molecules of water, followed by the elimination of one such molecule, although such a change appeared highly improbable. It was considered advisable, therefore, in order conclusively to prove the constitution of homoeriodictyol and related compounds, to have recourse to synthetical experiments.

If the formulæ suggested by Dr. Power and the present author for eriodictyol, homoeriodictyol, and hesperitin be correct, then these substances are 2 : 4 : 6-*trihydroxyphenyl* 3 : 4-*dihydroxystyryl ketone*, 2 : 4 : 6-*trihydroxyphenyl* 4-*hydroxy*-3-*methoxystyryl ketone*, and 2 : 4 : 6-*trihydroxyphenyl* 3-*hydroxy*-4-*methoxystyryl ketone* respectively. It was decided therefore to methylate the first-mentioned three substances, and to compare the fully methylated products with synthetically prepared 2 : 4 : 6-*trimethoxyphenyl* 3 : 4-*dimethoxystyryl ketone*. The results of the methylation of eriodictyol, homoeriodictyol, and hesperitin are recorded in the present paper, and it is shown that each of them yields 2 : 4 : 6-trimethoxyphenyl 3 : 4-dimethoxystyryl ketone and 2-hydroxy-4 : 6-dimethoxyphenyl 3 : 4-dimethoxystyryl ketone identical in all respects with these substances as prepared synthetically (see the following paper).

The correctness of the formulæ suggested by Power and Tutin for eriodictyol, homoeriodictyol, and hesperitin is therefore proved beyond question.

Naringenin, a hydrolytic product of the glucoside, naringin, was shown by Will (*Ber.*, 1885, **18**, 1311) to be related to hesperitin. On heating with aqueous potassium hydroxide, it undergoes hydrolysis in a manner similar to the latter compound, and yields phloroglucinol and *p*-hydroxycinnamic acid. Will therefore concluded (*Ber.*, 1887, **20**, 297) that naringenin was the phloroglucinyl ester of the above-mentioned acid. In view of the results recorded in the present paper concerning hesperitin, there can be no doubt that naringenin is also a ketone, namely, 2 : 4 : 6-*trihydroxyphenyl* 4-*hydroxystyryl ketone.*

In a previous communication (Power and Tutin, Trans., *loc. cit.*) a monomethyl ether of homoeriodictyol was described. A larger quantity of this substance has now been prepared, and it has been proved to be 2 : 6-*dihydroxy*-4-*methoxyphenyl* 4-*hydroxy*-3-*methoxystyryl ketone*. Similarly, when one methyl group is introduced into eriodictyol, it takes up the 4-position in the phenyl radicle, the product being a new isomeride of homoeriodictyol and hesperitin, namely, 2 : 6-*dihydroxy* - 4 - *methoxyphenyl* 3 : 4 - *dihydroxystyryl ketone.*

The observation of Perkin (*loc. cit.*) regarding the anomalous character of the sodium derivative of hesperitin has been confirmed, this substance appearing to have the formula $C_{16}H_{13}O_6Na,C_{16}H_{14}O_6$. On the other hand, the statement made by Perkin that the product of the action of acetic anhydride on hesperitin is a triacetyl derivative cannot be confirmed, it having been proved that the substance thus formed is *tetra-acetylhesperitin.*

EXPERIMENTAL.

Eriodictyol (2:4:6-*Trihydroxyphenyl* 3:4-*Dihydroxystyryl Ketone*).

A quantity (5 grams) of eriodictyol * was dissolved in alcohol, and an excess of methyl sulphate added, after which a concentrated alcoholic solution of potassium hydroxide was allowed to flow into the hot liquid at such a rate that the mixture was kept gently boiling. The liquid at first showed a tendency to darken, owing to the absorption of oxygen, but this soon ceased as methylation proceeded. Finally, the mixture assumed a dark red colour on the addition of the alkali, which only slowly disappeared. A further quantity of methyl sulphate was added, followed by more alkali, after which the mixture was kept for twenty minutes and then poured into water. The yellow product precipitated by this treatment was extracted by means of chloroform, the solution being washed, dried, and the solvent removed. The residue thus obtained was boiled with successive portions of dilute, aqueous potassium hydroxide so long as the decanted alkaline liquid was yellow in colour, after which the material insoluble in the alkali was washed and dissolved in alcohol. On inoculating the solution thus obtained with synthetic 2:4:6-trimethoxyphenyl 3:4-dimethoxystyryl ketone (see the following paper), crystallisation rapidly ensued. The product so obtained was identical in all respects with the synthetical compound just mentioned. It crystallised in stout, pale yellow prisms, and, when dried in the air, melted at 85°, but in the anhydrous state at 117·5°:

0·1747 † gave 0·4279 CO_2 and 0·1046 H_2O. C = 66·8; H = 6·4.

$C_{20}H_{22}O_6$ requires C = 67·0; H = 6·1 per cent.

The potassium hydroxide extracts which had been decanted from the crude 2:4:6-trimethoxyphenyl 3:4-dimethoxystyryl ketone were acidified, and the precipitated yellow product was crystallised from alcohol, in which it was rather sparingly soluble. Deep yellow leaflets were thus obtained, which melted at 154°, and were identical with the 2-hydroxy-4 : 6-dimethoxyphenyl 3 : 4-dimethoxystyryl ketone described in the following paper:

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* For an improved method of isolating eriodictyol, homoeriodictyol, and other phenolic substances from *Eriodictyon* leaves, compare Tutin and Clewer, Trans., 1909, **95**, 81.

† Anhydrous substance.

0·1279 gave 0·3099 CO_2 and 0·0680 H_2O. C = 66·1; H = 5·9.

$C_{19}H_{20}O_6$ requires 66·3; H = 5·8 per cent.

Monomethyleriodictyol (2 : 6-*Dihydroxy*-4-*methoxyphenyl* 3 : 4-*dihydroxystyryl ketone*).—Four grams of eriodictyol were dissolved in absolute alcohol, and to this solution was added one and a-half molecular proportions of methyl sulphate, which had just previously been washed with aqueous sodium carbonate and dried. Slightly more than the equivalent amount of sodium, dissolved in absolute alcohol, was then gradually introduced into the hot mixture. After removing the alcohol, the residue was dissolved in ether, washed with water, and then fractionally extracted by shaking with successive portions of an aqueous solution of sodium carbonate. The first few extractions removed only unchanged eriodictyol, which formed the greater part of the product, but on acidifying the alkaline liquids subsequently obtained, a yellow product separated, which partly crystallised on keeping. This was collected, well washed with alcohol, and then recrystallised from this solvent, in which it was but sparingly soluble. Almost colourless needles were thus obtained, which melted at 215°:

0·1284 gave 0·2995 CO_2 and 0·0583 H_2O. C = 63·6; H = 5·0.

$C_{16}H_{14}O_6$ requires C = 63·5; H = 4·6 per cent.

This substance was therefore a *monomethyleriodictyol*, and since it is not identical with either homoeriodictyol (2 : 4 : 6-trihydroxyphenyl 4-hydroxy-3-methoxystyryl ketone) or hesperitin (2 : 4 : 6-trihydroxyphenyl 3-hydroxy-4-methoxystyryl ketone), and the hydroxyl group in the 2(or 6)-position is known to be difficult of methylation, it must be 2 : 6-*dihydroxy*-4-*methoxyphenyl* 3 : 4-*dihydroxystyryl ketone*.

Monomethyleriodictyol dissolves in aqueous alkali hydroxides, giving at first a practically colourless solution, but after about thirty seconds the liquid suddenly becomes totally black. On acetylation, monomethyleriodictyol yields a *tetra-acetyl* derivative, which forms colourless needles, melting at 159°.

Homoeriodictyol (2 : 4 : 6-*Trihydroxyphenyl* 4-*Hydroxy*-3-*methoxystyryl Ketone*).

The methylation of homoeriodictyol by means of methyl sulphate and potassium hydroxide proceeded analogously to that of eriodictyol, with the exception that there was no tendency to absorb oxygen, and consequently a cleaner product was obtained. The methylated material was examined as above-described, when it readily yielded 2:4:6-trimethoxyphenyl 3:4-dimethoxystyryl ketone (m. p. 85° when air-dried; 117·5° when anhydrous), and 2-hydroxy-4:6-dimethoxyphenyl 3:4-dimethoxystyryl ketone (m. p. 154°).

Monomethylhomoeriodictyol (2:6-*Dihydroxy*-4-*methoxyphenyl* 4-*hydroxy*-3-*methoxystyryl ketone*).—Monomethylhomoeriodictyol, prepared by the action of methyl iodide on the crystalline sodium derivative of homoeriodictyol, was previously described by Power and Tutin (Trans., 1907, **91**, 895). A larger amount of this product has now been prepared by heating the above-mentioned sodium derivative with methyl iodide and methyl alcohol. The product thus obtained was dissolved in ether and freed from unchanged homoeriodictyol by extraction with dilute, aqueous sodium carbonate, after which the monomethylhomoeriodictyol was removed by shaking with a concentrated solution of this alkali. The product so obtained crystallised readily from alcohol in hard, yellow, wart-like masses, which melted at 142°.

On boiling monomethylhomoeriodictyol for several hours with 30 per cent. aqueous potassium hydroxide, hydrolysis occurred at the double linking, after which vanillin was readily isolated from the reaction mixture. It is evident from this, and considerations previously given, that the ONa group in the sodium derivative of homoeriodictyol, which is converted into methoxyl on treatment with methyl iodide, must occupy the 4-position in the phenyl group of the molecule. Monomethylhomoeriodictyol is therefore 2:6-*dihydroxy*-4-*methoxyphenyl* 4-*hydroxy*-3-*methoxystyryl ketone*.

Hesperitin (2:4:6-*Trihydroxyphenyl* 3-*Hydroxy*-4-*methoxystyryl Ketone*.)

Hesperitin, which is obtained by the hydrolysis of the glucoside, hesperidin, a constituent of the peel of the orange, lemon, and other related fruits, has been stated by Tiemann and Will (*Ber.*, 1881, **14**, 970) to be the phloroglucinyl ester of *iso*ferulic acid. As stated in the introductory portion of this paper, however, the accuracy of this conclusion was doubted by Power and Tutin, and the present author has therefore further investigated the question.

Hesperitin, as obtained from Schuchardt, was recrystallised from ethyl acetate, when it melted at 224°, but when mixed with homoeriodictyol, fusion occurred at 200°. The material so obtained, however, did not agree in its characters with the description of hesperitin as given by A. G. Perkin (Trans., 1898, **73**, 1037). Thus it formed pale yellow plates, which could not be distinguished by inspection from crystals of homoeriodictyol, it was practically tasteless,* and it dissolved in alkalis with a bright yellow colour. Perkin (*loc. cit.*), on the other hand, has described hesperitin as crystallising in almost colourless needles, possessing an intensely sweet taste, and dissolving in alkalis with, at the most, a faintly yellow colour. Nevertheless, the identity of the material employed by the present author with hesperitin cannot be doubted, inasmuch as the melting points of the compound itself and its acetyl derivative are in agreement with the corresponding constants given by Perkin for hesperitin and its acetyl derivative. Moreover, the substance yielded the abnormal sodium derivative, $C_{16}H_{13}O_6Na,C_{16}H_{14}O_6$, characteristic of hesperitin. (Found, Na = 3·8. Calc., Na = 3·8 per cent.)

Methylation of Hesperitin.

A quantity (1·5 grams) of hesperitin was methylated by means of potassium hydroxide and methyl sulphate in the manner previously described, when the reaction appeared to proceed precisely as in the case of homoeriodictyol. A good yield of product was obtained, which was readily separated into the two compounds similarly prepared from eriodictyol and its homologue, namely, 2-hydroxy-4 : 6-dimethoxyphenyl 3 : 4-dimethoxystyryl ketone (m. p. 154) and 2 : 4 : 6-trimethoxyphenyl 3 : 4-dimethoxystyryl ketone (m. p. 85° when air-dried; 117·5° when anhydrous).

Tetra-acetylhesperitin.—Half a gram of hesperitin was boiled for three hours with a considerable excess of acetic anhydride, after which the greater part of the solvent was removed and the mixture diluted with ether. After several hours, a crystalline substance separated in tufts of colourless prisms, which melted at 120°. After recrystallisation from alcohol, this substance melted at 127°, and was evidently identical with the compound similarly prepared by Perkin (*loc. cit.*), which he regarded as a triacetyl derivative. The number of acetyl groups in the compound were estimated as follows. A quantity of the substance was hydrolysed with dilute potassium hydroxide, the mixture then acidified with sulphuric acid, and the acetic acid removed by a current of steam and titrated:

0·2616 gave acetic acid equivalent to 0·0900 NaOH. $CO\cdot CH_3 = 36\cdot 9$.

$C_{16}H_{10}O_6(CO\cdot CH_3)_4$ requires $CO\cdot CH_3 = 36\cdot 6$ per cent.

It is evident therefore that this compound was *tetra-acetylhesperitin*, and not a triacetyl derivative. This conclusion is in harmony with the properties of the substance, for it was insoluble in cold dilute sodium hydroxide, which would not have been the case had it contained a hydroxyl group, all the groups of this nature present in hesperitin having phenolic properties.

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* Although hesperitin, when in the solid state, possesses no appreciable taste, its alcoholic solution is distinctly sweet.

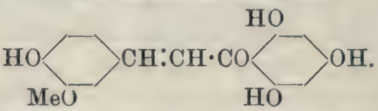
THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

CCXVII.—*The Synthesis of 2:4:6-Trimethoxyphenyl 3:4-Dimethoxystyryl Ketone. A Methyl Derivative of Eriodictyol, Homoeriodictyol, and Hesperitin.*

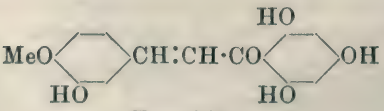
By FRANK TUTIN and FREDERIC WILLIAM CATON.

SOME time ago Power and Tutin (*Proc. Amer. Pharm. Assoc.*, 1906, **54**, 352) isolated from the leaves of *Eriodictyon Californicum* (Hooker and Arnott), Greene, two crystalline substances of phenolic nature, which were designated eriodictyol and homoeriodictyol respectively. Eriodictyol was shown to possess the formula $C_{15}H_{12}O_6$, whilst homoeriodictyol was found to be isomeric with hesperitin, having the formula $C_{16}H_{14}O_6$.

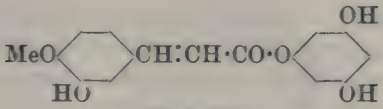
In a subsequent communication (Power and Tutin, Trans., 1907, **91**, 887) results were recorded which indicated that homoeriodictyol possesses the following constitutional formula:



The amount of eriodictyol at that time available did not permit of many experiments being conducted with this substance, but the conclusion was drawn that it differed from its homologue only by having a hydroxyl in the place of the methoxyl group. It was furthermore suggested from certain similarities in the properties of homoeriodictyol and hesperitin that these two substances differed only in the relative positions of the hydroxyl and methoxyl groups in the catechol part of the molecule, and that, consequently, the constitutional formula hitherto assigned to hesperitin was incorrect (Tiemann and Will, *Ber.*, 1881, **14**, 970; Perkin, Trans., 1898, **73**, 1037):



Hesperitin
(Power and Tutin).

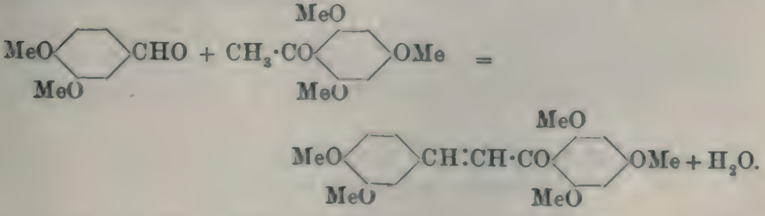


Hesperitin
(Tiemann and Will).

The above conclusions have now all been confirmed, inasmuch as, in the preceding paper, it is shown that eriodictyol, homoeriodictyol, and hesperitin each yield the same product when fully methylated. Final and conclusive proof of the structure of these compounds was, however, desirable, and it appeared that this could best be obtained by the synthesis of the fully methylated product.

If the views previously expressed regarding the constitution of eriodictyol, homoeriodictyol, and hesperitin be correct (Power and Tutin, Trans, *loc. cit.*), then these substances are 2:4:6-trihydroxyphenyl 3:4-dihydroxystyryl ketone, 2:4:6-trihydroxyphenyl 4-hydroxyl-3-methoxystyryl ketone, and 2:4:6-trihydroxyphenyl 3-hydroxy-4-methoxystyryl ketone respectively. It was therefore sought to synthesise 2:4:6-trimethoxyphenyl 3:4-dimethoxystyryl ketone in order that it might be compared with the compound obtained on fully methylating the naturally occurring substances under consideration. This has been accomplished, and the synthetical compound has been found to be in all respects identical with the product obtained from the three substances occurring in nature, thus affording conclusive proof of the constitution of the latter compounds.

2:4:6-Trimethoxyacetophenone was prepared by the interaction of acetyl chloride and phloroglucinol trimethyl ether in the presence of anhydrous ferric chloride, and this ketone was condensed with vanillin methyl ether by means of "molecular" sodium in a manner similar to that employed by Perkin and Weizmann (Trans., 1906, **89**, 1649), when 2:4:6-*trimethoxyphenyl* 3:4-*dimethoxystyryl ketone* resulted in good yield:



This substance gave, on heating with aluminium chloride, a hydroxytetramethoxy-compound, which melted at practically the same temperature as 2-hydroxy-4:6-dimethoxyphenyl 3:4-dimethoxystyryl ketone described by Kostanecki (*Ber.*, 1904, **37**, 793).

The present authors, however, were unable to obtain from the substance prepared by them the acetyl derivative described by Kostanecki. Nevertheless, it is considered certain that the hydroxytetramethoxy-compound obtained by the present authors is identical with that prepared by Kostanecki, inasmuch as the latter author has shown that a methoxyl group in the phloroglucinol nucleus situated in the 2-position with respect to the side-chain is most easily hydrolysed by aluminium chloride.

2:4:6-Trimethoxyacetophenone was prepared by Kostanecki (*Ber.*, 1899, **32**, 2262) in the manner already mentioned, but it had previously been stated by Friedländer and Schnell (*Ber.*, 1897, **30**, 2150) to result from the interaction of phloroglucinol trimethyl ether and acetyl chloride in the presence of aluminium chloride. The present authors, however, could succeed in preparing it only by Kostanecki's method, and, when employing that of the earlier investigators, obtained a *hydroxydiacetyldimethoxybenzene*, $C_{12}H_{14}O_5$.

EXPERIMENTAL.

Methylation of Phloroglucinol.

Will (*Ber.*, 1888, **21**, 603) obtained phloroglucinol trimethyl ether by the action of sodium and methyl iodide on the dimethyl ether, the latter being prepared by passing anhydrous hydrogen chloride into a methyl-alcoholic solution of phloroglucinol. The present authors, with the endeavour to simplify this process, sought to obtain the trimethyl ether by the direct methylation of phloroglucinol with methyl sulphate and potassium hydroxide. This method, however, did not give satisfactory yields of the desired substance, a considerable part of the material being converted into a neutral oily product. The latter distilled at 140—145°/13 mm., or at 258—266° under the ordinary pressure. It was unchanged by further treatment with methyl sulphate and potassium hydroxide, but was not further investigated. The method employed by Will (*loc. cit.*) was therefore adopted, but with the employment of methyl sulphate instead of methyl iodide. In this way satisfactory yields of phloroglucinol trimethyl ether (m. p. 52°) were obtained.

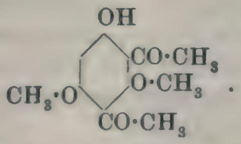
Action of Acetyl Chloride and Aluminium Chloride on Phloroglucinol Trimethyl Ether.

Friedländer and Schnell (*loc. cit.*) treated phloroglucinol trimethyl ether with acetyl chloride and aluminium chloride, and obtained thereby 2-hydroxy-4:6-dimethoxyacetophenone and the corresponding trimethoxy-ketone. The present authors, however, when employing the method of these investigators, could isolate from the reaction mixture only a small amount of 2-hydroxy-4:6-dimethoxyacetophenone, unchanged phloroglucinol trimethyl ether, and a *hydroxydiacetyldimethoxybenzene*, $C_{12}H_{14}O_5$, no matter how the conditions of the experiment were varied.

A quantity (11·5 grams) of phloroglucinol trimethyl ether was dissolved in carbon disulphide, 6 grams of acetyl chloride added, and then 10 grams of powdered aluminium chloride gradually introduced. After heating the mixture for one hour the solvent was decanted, and the residue decomposed with ice and hydrochloric acid. The product so obtained was dissolved in ether and shaken with a solution of potassium hydroxide, which removed the greater part of the material. The neutral product remaining in the ether consisted almost entirely of unchanged phloroglucinol trimethyl ether. The alkaline extracts were acidified, and the precipitated product was crystallised, first from ether, and then from alcohol, when it formed long, slender prisms, melting at 127—128°:

0·1090 gave 0·2407 CO_2 and 0·0583 H_2O. C=60·2; H=5·9.
0·1130 „ 0·2491 CO_2 „ 0·0595 H_2O. C=60·1; H=5·9.
0·1316 „ 0·2924 CO_2 „ 0·0714 H_2O. C=60·6; H=6·0.
$OH{\cdot}C_6H_2(OMe)_2(CO{\cdot}CH_3)$ requires C=61·2; H=6·1 per cent.
$OH{\cdot}C_6H(OMe)_2(CO{\cdot}CH_3)_2$ „ C=60·5; H=5·9 „
$OH{\cdot}C_6(OMe)_2(CO{\cdot}CH_3)_3$ „ C=60·0; H=5·7 „

These analyses indicate that the substance under consideration was a *hydroxydiacetyldimethoxybenzene*, $OH{\cdot}C_6H(OMe)_2(CO{\cdot}CH_3)_2$, and this conclusion was subsequently confirmed by the analysis of its *benzoyl* derivative. No direct proof of the constitution of the diketone was obtained, but it would appear most probable that it is represented as follows:



This formula is preferred to the other possible one, as it is known that 2:4:6-trimethoxyacetophenone, which must first be formed, readily yields 2-hydroxy-4:6-dimethoxyacetophenone in the presence of aluminium chloride, and a second acetyl group, when entering the nucleus of the latter ketone, would assuredly enter the para-position with respect to the hydroxyl group.

Hydroxydiacetyldimethoxybenzene is sparingly soluble in ether, and moderately so in alcohol. It did not lose either of the methyl groups when treated with anhydrous ferric chloride or with aluminium chloride, and attempts to introduce a third acetyl group into the nucleus of it were unsuccessful.

Acetoxydiacetyldimethoxybenzene, $OAc\cdot C_6H(OMe)_2(CO\cdot CH_3)_2$.—The *acetyl* derivative of the above-described compound was prepared by means of acetic anhydride. It crystallised from its concentrated solution in this solvent, and was purified by recrystallisation from benzene. *Acetoxydiacetyldimethoxybenzene* forms well-defined prisms, melting at 150·5°:

0·1132 gave 0·2409 CO_2 and 0·0572 H_2O. C = 60·0; H = 5·6.
$C_{14}H_{16}O_6$ requires C = 60·0; H = 5·7 per cent.

This substance cannot be crystallised from ordinary alcohol or other hydrous solvents, as it is rapidly hydrolysed when dissolved in such liquids.

Benzoyloxydiacetyldimethoxybenzene, $OBz\cdot C_6H(OMe)_2(CO\cdot CH_3)_2$.—This compound was prepared by the Schotten-Baumann reaction. It crystallised from benzene in cubes, and from absolute alcohol in slender prisms, melting at 179°:

0·1132 gave 0·2768 CO_2 and 0·0551 H_2O. C = 66·7; H = 5·4.
$C_{19}H_{22}O_6$ requires C = 66·7; H = 5·3 per cent.

The analysis of this compound conclusively confirms the results obtained by the analysis of the original hydroxy-diketone, inasmuch as the related compounds containing one and three acetyl groups would require C = 65·6 and C = 68·0 per cent. respectively.

Hydroxydiacetyldimethoxybenzenephenylhydrazone.—One gram of hydroxydiacetyldimethoxybenzene was dissolved in a small amount of alcohol, and slightly more than two molecular proportions of freshly distilled phenylhydrazine dissolved in acetic acid added. The mixture was heated on a water-bath for a quarter of an hour, when, after concentration, a crystalline product separated. This was collected, and crystallised many times, first from acetic acid, and subsequently from a mixture of ethyl acetate and alcohol, when the melting point gradually rose from 215° to 230°, the product finally obtained forming hexagonal prisms melting sharply at the latter temperature:

0·0927 gave 0·2248 CO_2 and 0·0529 H_2O. C = 66·1; H = 6·3.
0·1012 ,, 8·4 c.c. N_2 (moist) at 19° and 753 mm. N = 9·4.
$C_{18}H_{20}O_4N_2$ requires C = 65·8; H = 6·1; N = 8·5 per cent.

This compound was therefore a *monophenylhydrazone* of hydroxydiacetyldimethoxybenzene.

The original ethereal mother liquors from the hydroxydiacetyldimethoxybenzene yielded a small amount of a substance which, when crystallised from alcohol, melted at 80°:

0·0754 gave 0·1685 CO_2 and 0·0425 H_2O. C = 61·2; H = 6·3.
$C_{10}H_{12}O_4$ requires C = 61·2; H = 6·1 per cent.

This substance was evidently 2-hydroxy-4 : 6-dimethoxyacetophenone, described by Friedländer and Schnell (*loc. cit.*).

Since no trimethoxyacetophenone could be obtained by means of the aluminium chloride reaction, recourse was had to the use of sublimed ferric chloride (Kostanecki, *Ber.*, 1899, **32**, 2261). By this means a good yield of product was obtained, which consisted largely of 2 : 4 : 6-trimethoxyacetophenone (m. p. 99—100°), but contained a little of the previously described hydroxydiacetyldimethoxybenzene.

Condensation of 2 : 4 : 6-*Trimethoxyacetophenone with Vanillin Methyl Ether. Formation of* 2 : 4 : 6-*Trimethoxyphenyl* 3 : 4-*Dimethoxystyryl Ketone.*

Vanillin was methylated by means of methyl sulphate in the manner described by Perkin and Weizmann (Trans., 1906, **89**, 1649), when vanillin methyl ether was readily obtained. One molecular proportion of the latter compound was then heated in dry ethereal solution with equivalent amounts of 2 : 4 : 6-trimethoxyacetophenone and finely divided sodium.* Hydrogen was slowly evolved, and, after six hours, a yellow solid commenced to separate. When the reaction was complete, which was after about twenty-four hours heating, the ether was decanted, and the residue dissolved in benzene and washed with water. Considerable difficulty was originally experienced in causing the yellow, viscid residue obtained on evaporating the benzene to crystallise, but this was eventually effected from alcoholic solution, after which subsequent batches of material quickly crystallised on inoculating with the solid first obtained. 2 : 4 : 6-*Trimethoxyphenyl* 3 : 4-*dimethoxystyryl ketone* forms stout, pale yellow prisms, which contain one molecule of alcohol of crystallisation, and melt at 85°. The anhydrous substance melts at 117·5° :

0·1158 † gave 0·2778 CO_2 and 0·1158 H_2O. C = 65·4 ; H = 7·1.
0·1436 ‡ „ 0·3512 CO_2 „ 0·0796 H_2O. C = 66·7 ; H = 6·1.
1·0010,† on heating at 100°, lost 0·1140 EtOH. EtOH = 11·4.
$C_{20}H_{22}O_6$,EtOH requires C = 65·3 ; H = 6·9 ; EtOH = 11·4 per cent.
$C_{20}H_{22}O_6$ requires C = 67·0 ; H = 6·1 per cent.

2 : 4 : 6-Trimethoxyphenyl 3 : 4-dimethoxystyryl ketone is very readily soluble in benzene, xylene, chloroform, or acetic acid, moderately so in alcohol or carbon disulphide, and almost insoluble in ether or petroleum. It also dissolves readily in moderately concentrated hydrochloric or sulphuric acids, yielding deep red

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* Prepared by violently shaking molten sodium under xylene, the latter being subsequently removed by the addition of pure ether, and decantation.

† Air-dried.

‡ Anhydrous substance.

solutions. It distils without decomposition at 325°/13 mm., solidifying to a yellow, vitreous mass.

A quantity of the ketone was heated for five hours with a large excess of a concentrated alcoholic solution of potassium hydroxide. The greater part of the material was recovered unchanged after this treatment, but some veratric acid was isolated from the reaction mixture. It thus appears that, under the influence of potassium hydroxide, the ketone in question is attacked at the double linking, just as has been shown, in the preceding paper, to be the case with monomethylhomoeriodictyol. The first product of this change is, doubtless, vanillin methyl ether, which yields the veratric acid by the further action of the alkali.

Action of Aluminium Chloride on 2 : 4 : 6-*Trimethoxyphenyl* 3 : 4-*Dimethoxystyryl Ketone.*

With the endeavour to remove methyl groups from the above-described ketone, in order to see if, in this way, homoeriodictyol could be obtained, the effect of ferric and aluminium chlorides on the pentamethoxy-compound was investigated. Ferric chloride was quite without action on it, but when heated with aluminium chloride it slowly lost one methyl group. The change was by no means complete, even after many hours' heating, but the hydrolysed product was readily separated from the unchanged material by boiling the mixture with successive portions of dilute aqueous potassium hydroxide. The alkaline liquids so obtained yielded, on acidification, a yellow compound, which crystallised very readily from alcohol in deep golden-coloured plates, melting at 154°:

0·1122 gave 0·2724 CO_2 and 0·0584 H_2O. C = 66·2; H = 5·8.

$C_{19}H_{20}O_6$ requires C = 66·3; H = 5·8 per cent.

This compound is doubtless identical with the 2-hydroxy-4 : 6-dimethoxyphenyl 3 : 4-dimethoxystyryl ketone (m. p. 157°) prepared in another way by Kostanecki (*Ber.*, 1904, **37**, 793), but the present authors were unable to obtain the crystalline acetyl derivative described by him, although several attempts were made.

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CCXVIII.—*The Molecular Complexity, in the Liquid State, of Tervalent Nitrogen Compounds.*

By William Ernest Stephen Turner and Ernest Wyndham Merry.

In a review of the possible causes of association in the amides by Dr. A. N. Meldrum and one of us (Trans., 1908, **93**, 876), it was suggested that the association observed might well be due to the presence of the tervalent nitrogen atom or the oxygen atom of the group $\cdot CO \cdot NH_2$, and the observations recorded in this communication were, in the main, carried out in order to test this suggestion.

Evidence bearing directly on the problem should be obtainable by an examination of the molecular complexity of the amines, for in these substances the nitrogen atom can pass with great readiness from the ter- to the quinque-valent state. Such data as existed at the beginning of the work were but meagre, consisting of determinations, either in solution or in the liquid state, of the molecular weight of aniline, two or three of its derivatives, and of the toluidines (Auwers and Pelzer, *Zeitsch. physikal. Chem.*, 1897, **23**, 449; Auwers and Dohrn, *ibid.*, 1899, **30**, 542; Dutoit and Friderich, *Compt. rend.*, 1900, **130**, 327). It is well known, however, and our research confirms the fact, that the molecular association of an aromatic substance is either considerably less than in the corresponding aliphatic compound, or is non-existent. We decided accordingly, whilst including a number of aromatic substances, to make a study of the aliphatic amines.

The research was extended, however, beyond a comparison of the amines and amides, and was made to include a survey of other nitrogen-containing compounds. Of these, some, notably aceto-, propio-, butyro-, and benzo-nitrile, had already been examined by several investigators (Ramsay and Shields, Trans., 1893, **63**, 1089; Dutoit and Friderich, *loc. cit.*; Guye and Baud, *Arch. Sci. phys. nat.*, 1901, [iv], **11**, 449; Renard and Guye, *J. Chim. phys.*, 1907, **5**, 97), although their results do not in all cases agree as well as might be expected. We have included in our work redeterminations with these four substances, but have not given full results in each case.

As regards the nitro-compounds, Ramsay and Shields (*loc. cit.*) have proved, by a comparison of nitroethane and nitrobenzene, that aliphatic nitro-compounds are associated, whilst aromatic compounds are non-associated. The observations on this class of substances we have not extended, but the possibility of association connected with the nitroso-group, as revealed by the tendency of a few derivatives of hydrocarbons to form double molecules at low temperatures (Piloty, *Ber.*, 1898, **31**, 452; Bamberger and Rising, *Ber.*, 1901, **34**, 3877), attracted us to examine three nitrosoamines, of which dimethylnitrosoamine is of particular interest on account of its considerable conductivity, solvent power, and dielectric constant (Walden, *Zeitsch. physikal. Chem.*, 1903, **46**, 103). From the high value of the dielectric constant we expected to find association.

The determination of the molecular complexities in the liquid state, rather than in solution, was attended by certain advantages, for our results render it possible to make a comparison, in some cases, with the extent of association in solution; and we have also been able to include a number of substances the solubilities of which in benzene and similar solvents are very slight, the advantage of being able to include formamide being considerable. As far as possible, the experiments have been carried out over the same range of temperatures.

Against these advantages, we have to set off the fact that the calculation and interpretation of the results by the Ramsay and Shields' method, which has been used in its original form, is open to objection, and our own determinations support those of Dutoit and Friderich and of Guye and his pupils in demonstrating that the Ramsay and Shields' formula can only be applied within somewhat circumscribed limits. We have not been able, owing to lack of data in most cases, to employ any of the alternative methods of determining the molecular complexity, such as have been suggested by Ramsay (*Proc. Roy. Soc.*, 1894, **56**, 175) and Walden (*Zeitsch. physikal. Chem.*, 1909, **65**, 184).

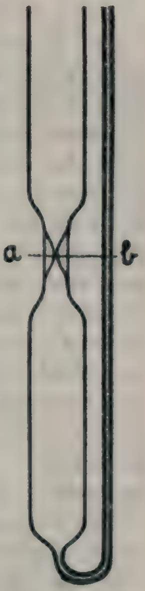
EXPERIMENTAL.

The measurement of surface tension was carried out in an apparatus of the U-tube type, the capillaries used in the construction being previously carefully tested and calibrated at different points. In form, the apparatus was very similar to that employed by Hewitt and Winmill (Trans., 1907, **91**, 441)—reference to their diagram will serve to explain our arrangement—but differed from it in two respects: the capillary tube was backed by enamel, and, more important still, the end of the capillary tube, to the extent of about one inch, was bent sharply downwards, and a piece of quill tubing of the same diameter fused on to it, this added tube being bent sharply upwards so as to be parallel both with the capillary and with the wide limb of the U-tube. The object of this elbow of quill tubing was twofold. It served, in the first place, as a trap for particles falling from the rubber connexions, and, in the second place, as a reservoir into which liquid could be transferred from the capillary.

Constant temperatures were obtained by the use of large baths and a carefully regulated flame. At the higher temperatures we employed a bath of paraffin wax (m. p. 60°), finding it much preferable to concentrated sulphuric acid, and we were able to use it at temperatures up to 210°.

In most of the experiments, the air was removed from the apparatus by exhaustion to a low pressure, although it has been shown by Renaud and Guye (*loc. cit.*) that unless the substance is easily oxidisable, measurements of the surface tension made both in presence and in absence of air agree to within about ½ per cent.

At each temperature, three readings of the capillary rise were made by means of a reading micrometer, the differences never amounting to more than four hundredths of a millimetre. A fresh surface was obtained for each reading by tilting the tube and allowing liquid to run from the capillary into the elbow of quill tubing. The substances of high melting point could not be treated in this way, and in these cases a fresh surface was obtained by temporarily forcing the liquid from the capillary into the wide tube. Two independent series of determinations of the surface tension were made with each substance, in many cases by employing two tubes and placing them side by side in the same bath.



The density determinations were mainly made in specific gravity bottles of 10 c.c. capacity, calibrated at five or six different temperatures between 20° and 90°, so that the volumes at other temperatures could be deduced. At the higher temperatures considerable difficulty was experienced in using this form of pyknometer, and the simple form shown in the diagram was devised and employed, the narrow tubing being capillary of 1—1·5 mm. diameter of quill tubing of about the same bore. The cup was charged with the solid, and the pyknometer transferred to the heating bath. The liquid level was adjusted by air pressure to the mark *b*, excess above the level *a* removed by fine capillary tubes, and the cup wiped out before weighing. All densities are compared with that of water at 4°.

With the exception of benzamide and salicylamide, the materials were obtained by purchase, mainly from Kahlbaum, and all were subjected to purification save a pure specimen of phenylhydrazine obtained from Kahlbaum.

The liquid amines were treated with solid sodium or potassium hydroxide, and afterwards distilled, benzyl-, dibenzyl-, and triamylamine under diminished pressure, the others under atmospheric pressure. Distillates of constant, or almost constant, boiling point were obtained and used throughout. Diphenylamine and tribenzylamine were crystallised from alcohol until of constant melting point. Wherever possible, the densities obtained were compared with those of other investigators. The density of the aniline employed agreed exactly with that found by Brühl (*Zeitsch. physikal. Chem.*, 1895, **16**, 193); and those of propyl-, dipropyl-, and tripropyl-amine were in very close agreement with the numbers given by Perkin (Trans., 1889, **55**, 693).

The nitrosoamines (from Schuchardt) were treated as follows: phenylmethylnitrosoamine with freshly heated sodium sulphate, the two others with recently ignited potassium carbonate, and subsequently distilled under diminished pressure.

Of the nitriles, acetonitrile, benzonitrile, phenylacetonitrile, and *m*-toluonitrile were treated with phosphoric oxide and afterwards distilled, the acetonitrile under atmospheric, the others under diminished pressure. Propio-, butyro-, and *iso*butylaceto-nitrile were kept over sodium sulphate, and then distilled under atmospheric pressure. Lacto-, mandelo- and *o*-toluo-nitrile were merely distilled under diminished pressure. The melting point of the *p*-toluonitrile was 28·4°, and the substance was used without further purification. The densities at 20° of acetonitrile and benzonitrile agreed very closely with the values found by Brühl (*loc. cit.*), but those of propio- and *iso*butylaceto-nitrile were a little higher, that of phenylacetonitrile a little lower, than Brühl found.

The formamide was well dried over sodium sulphate and afterwards distilled under diminished pressure. Its density at 20° was in good agreement with that given by Brühl. The other amides, the anilides and urethanes were purified by methods already described (Meldrum and Turner, this vol., p. 1607). At the conclusion of the surface-tension measurements, the melting points of the salicylamide and phenylacetamide were tested, and found to agree exactly with those of the original substances.

In addition to the amides on which we have been successful in making measurements, we endeavoured to bring into the scope of the work a number of diamides and ethyl oxamate, but found them all unstable. Carbamide decomposed at its melting point; ammonia from malonamide could be detected even before melting; whilst ethyl oxamate, when gradually heated, gave ammonia at 130°.

Neither could we find a suitable solvent for these substances. Their insolubility in benzene, ether, etc., is well known. Lachman (*Zeitsch. physikal. Chem.*, 1897, **22**, 170) found that ethyl oxamate is soluble in methyl oxalate, and, in this solvent, gave molecular-weight values indicative of decided association. We used methyl oxalate, ethyl oxalate, diphenylamine, and phenylurethane in attempts to dissolve carbamide, oxamide, malonamide, and succinamide, but found all these amides either insoluble or only slightly soluble. We possess indirect evidence, however, showing that these substances should be classed as associated.

In the following tables are recorded the molecular weight of the substance, the temperature (t), the capillary rise in cm. (h), the radius of the tube in mm. (r), the density (ρ), the surface tension (γ), the values k_1 and k_2 of the Ramsay and Shields' constants calculated from the separate experiments, k, the mean values, and the degree of association (x).

In the case of formamide the mean values of k are derived from four sets of experiments.

Amines.

n-*Propylamine* (M.W. = 59).

t°.	h.	r.	ρ.	γ.	k_1.	k_2.	k.	x.
10°	3·646	0·1779	0·7271	23·13	—	—	—	—
20	3·506	0·1779	0·7185	21·98	1·83	1·85	1·84	1·24
30	3·368	0·1779	0·7081	20·81	1·83	1·84	1·835	1·24
45	3·164	0·1780	0·6894	19·04	1·82	1·86	1·84	1·24

Dipropylamine (M.W. = 101).

20°	3·462	0·1779	0·7390	22·32	—	—	—	—
30	3·334	0·1799	0·7299	21·23	2·42	2·14	2·28	0·90
45	3·152	0·1780	0·7164	19·72	2·27	2·31	2·29	0·89
60	2·962	0·1780	0·7025	18·17	2·37	2·33	2·35	0·86

Tripropylamine (M.W. = 143).

20°	3·342	0·1850	0·7571	22·96	—	—	—	—
30	3·238	0·1851	0·7493	22·03	2·56	2·43	2·495	0·78
45	3·079	0·1851	0·7373	20·61	2·64	2·63	2·635	0·72
60	2·919	0·1851	0·7252	19·22	2·63	2·65	2·64	0·72
75	2·760	0·1851	0·7130	17·87	2·61	2·65	2·63	0·72

iso*Amylamine* (M.W. = 87).

20°	3·462	0·1851	0·7505	23·59	—	—	—	—
30	3·352	0·1851	0·7417	22·57	1·99	1·92	1·955	1·13
45	3·184	0·1851	0·7277	21·04	2·03	2·03	2·03	1·07
60	3·018	0·1851	0·7128	19·53	2·00	2·03	2·015	1·08

Triamylamine (M.W. = 227).

20°	3·399	0·1851	0·7859	24·25	—	—	—	—
30	3·310	0·1851	0·7790	23·41	3·09	3·12	3·105	0·56
45	3·172	0·1851	0·7676	22·11	3·18	3·11	3·145	0·55
60	3·034	0·1851	0·7568	20·85	3·14	3·07	3·115	0·56
75	2·892	0·1851	0·7461	19·59	3·20	3·17	3·185	0·54

Amines (continued).

Diphenylamine (M.W. = 169).

t°.	h.	r.	ρ.	γ.	k_1.	k_2.	k.	x.
60°	4·268	0·1777	1·0547	39·23	—	—	—	—
75	4·150	0·1778	1·0435	37·77	2·37	2·66	2·515	0·77
90	4·023	0·1778	1·0326	36·23	2·55	2·46	2·505	0·78
105	3·890	0·1778	1·0217	34·66	2·63	2·55	2·59	0·74

Benzylamine (M.W. = 107).

t°.	h.	r.	ρ.	γ.	k_1.	k_2.	k.	x.
20°	4·388	0·1850	0·9813	39·07	—	—	—	—
30	4·298	0·1850	0·9727	37·94	2·09	2·07	2·08	1·03
45	4·155	0·1850	0·9597	36·17	2·19	2·05	2·12	1·00
60	4·015	0·1850	0·9463	34·49	2·12	2·05	2·085	1·03
75	3·872	0·1850	0·9338	32·81	2·28	2·17	2·225	0·97

Dibenzylamine (M.W. = 197).

t°.	h.	r.	ρ.	γ.	k_1.	k_2.	k.	x.
20°	4·362	0·1850	1·0276	40·68	—	—	—	—
30	4·280	0·1850	1·0199	39·61	2·90	2·71	2·805	0·66
45	4·150	0·1850	1·0083	38·01	2·92	2·78	2·85	0·64
60	4·026	0·1850	0·9963	36·40	2·93	2·82	2·875	0·63
75	3·894	0·1850	0·9844	34·79	3·01	2·99	3·00	0·59

Tribenzylamine (M.W. = 287).

t°.	h.	r.	ρ.	γ.	k_1.	k_2.	k.	x.
95°	3·707	0·1850	0·9912	33·34	—	—	—	—
105	3·628	0·1850	0·9850	32·43	3·42	3·40	3·41	0·49
120	3·504	0·1850	0·9741	30·97	3·59	3·46	3·525	0·47
135	3·378	0·1851	0·9632	29·54	3·57	3·59	3·58	0·46

Phenylhydrazine (M.W. = 108).

t°.	h.	r.	ρ.	γ.	k_1.	k_2.	k.	x.
20°	4·572	0·1850	1·0978	45·55	—	—	—	—
30	4·480	0·1850	1·0899	44·31	2·18	2·16	2·17	0·97
45	4·322	0·1850	1·0777	42·27	2·47	2·27	2·37	0·85
60	4·179	0·1850	1·0653	40·40	2·23	2·16	2·195	0·95

Dimethylnitrosoamine (M.W. = 74).

t°.	h.	r.	ρ.	γ.	k_1.	k_2.	k.	x.
20°	4·269	0·1850	1·0059	38·97	—	—	—	—
30	4·173	0·1850	0·9965	37·73	1·74	1·75	1·745	1·34
45	4·020	0·1850	0·9813	35·80	1·85	1·86	1·855	1·22
60	3·858	0·1850	0·9654	33·80	1·94	1·93	1·935	1·15
75	3·692	0·1850	0·9491	31·80	1·97	1·92	1·945	1·14

Diethylnitrosoamine (M.W. = 102).

t°.	h.	r.	ρ.	γ.	k_1.	k_2.	k.	x.
20°	3·838	0·1850	0·9422	32·81	—	—	—	—
30	3·758	0·1850	0·9331	31·82	1·79	1·77	1·78	1·30
45	3·628	0·1850	0·9197	30·28	1·90	1·89	1·895	1·18
60	3·490	0·1851	0·9061	28·71	1·97	2·00	1·985	1·10
75	3·350	0·1851	0·8919	27·13	2·01	2·02	2·015	1·08

Phenylmethylnitrosoamine (M.W. = 136).

t°.	h.	r.	ρ.	γ.	k_1.	k_2.	k.	x.
20°	4·394	0·1850	1·1275	44·96	—	—	—	—
30	4·310	0·1850	1·1187	43·75	2·38	2·30	2·34	0·86
45	4·182	0·1850	1·1055	41·95	2·40	2·43	2·415	0·82
60	4·048	0·1850	1·0919	40·11	2·49	2·51	2·50	0·78
75	3·916	0·1850	1·0782	38·31	2·45	2·48	2·465	0·80
90	3·782	0·1850	1·0644	36·53	2·47	2·55	2·51	0·78

Nitriles.

Lactonitrile (M.W. = 71).

t°.	h.	r.	ρ.	γ.	k_1.	k_2.	k.	x.
20°	4·059	0·1850	0·9877	36·38	—	—	—	—
30	3·989	0·1850	0·9788	35·43	1·27	1·24	1·255	2·21
45	3·879	0·1850	0·9656	33·99	1·31	1·33	1·32	2·04
60	3·765	0·1850	0·9525	32·54	1·35	1·30	1·325	2·03

Butyronitrile (M.W. = 69).

20°	3·892	0·1780	0·7936	26·97	—	—	—	—
30	3·780	0·1780	0·7842	25·88	1·73	1·70	1·715	1·38
45	3·608	0·1779	0·7701	24·25	1·77	1·79	1·78	1·30
60	3·431	0·1779	0·7556	22·62	1·78	1·77	1·775	1·31

iso*Butylacetonitrile* (M.W. = 97).

20°	3·637	0·1850	0·8038	26·53	—	—	—	—
30	3·548	0·1850	0·7955	25·61	1·80	1·81	1·805	1·27
45	3·410	0·1851	0·7827	24·23	1·83	1·85	1·84	1·24
60	3·268	0·1851	0·7699	22·84	1·89	1·87	1·88	1·20

Benzonitrile (M.W. = 103).

20°	4·407	0·1776	1·0051	38·59	—	—	—	—
30	4·315	0·1777	0·9974	37·51	1·93	1·95	1·94	1·14
45	4·176	0·1777	0·9831	35·78	2·03	2·08	2·055	1·05
60	4·010	0·1778	0·9692	33·89	2·32	2·25	2·285	0·89

Phenylacetonitrile (M.W. = 117).

20°	4·488	0·1850	1·0157	41·36	—	—	—	—
30	4·404	0·1850	1·0076	40·27	2·09	2·07	2·08	1·03
45	4·276	0·1850	0·9939	38·56	2·14	2·13	2·135	0·99
60	4·136	0·1850	0·9792	36·75	2·32	2·29	2·315	0·88

Mandelonitrile (M.W. = 133).

20°	4·515	0·1776	1·1165	43·91	—	—	—	—
30	4·450	0·1776	1·1086	42·98	1·78	1·87	1·825	1·25
45	4·346	0·1776	1·0966	41·52	1·87	1·89	1·88	1·20
60	4·234	0·1777	1·0844	40·02	1·96	1·93	1·945	1·14

o-*Toluonitrile* (M.W. = 117).

20°	4·189	0·1850	0·9955	37·84	—	—	—	—
30	4·100	0·1850	0·9863	36·70	2·21	2·21	2·21	0·94
45	3·961	0·1850	0·9737	35·00	2·25	2·33	2·29	0·89
60	3·809	0·1850	0·9596	33·17	2·45	2·27	2·36	0·85
75	3·656	0·1850	0·9481	31·46	2·39	2·32	2·355	0·85

m-*Toluonitrile* (M.W. = 117).

20°	4·089	0·1778	1·0316	36·79	—	—	—	—
30	4·012	0·1778	1·0235	35·81	1·84	1·84	1·84	1·24
45	3·890	0·1778	1·0122	34·34	1·91	1·91	1·91	1·17
60	3·760	0·1778	0·9997	32·78	2·03	1·99	2·01	1·08
75	3·624	0·1779	0·9872	31·22	2·07	2·05	2·06	1·04

p-*Toluonitrile* (M.W. = 117).

30°	4·112	0·1850	0·9785	36·51	—	—	—	—
45	3·978	0·1850	0·9640	34·80	2·22	2·21	2·215	0·94
60	3·846	0·1850	0·9512	33·20	2·13	2·22	2·175	0·96
75	3·701	0·1850	0·9390	31·54	2·29	2·17	2·23	0·93

Amides.

Formamide (M.W. = 45).

t°.	*h*.	*r*.	ρ.	γ.	k_1.	k_2.	*k*.	*x*.
20°	5·812	0·1772	1·1350	57·35	—	—	—	—
30	5·770	0·1772	1·1267	56·51	0·65	0·61	0·63	6·18
45	5·704	0·1773	1·1142	55·27	0·64	0·65	0·66	5·76
60	5·634	0·1773	1·1015	53·94	0·73	0·73	0·74	4·85
75	5·529	0·1773	1·0892	52·36	0·93	0·94	0·95	3·34

Acetamide (M.W. = 59).

85°	4·300	0·1850	0·9986	38·96	—	—	—	—
95	4·226	0·1850	0·9904	37·98	1·18	1·14	1·16	2·47
105	4·147	0·1850	0·9822	36·96	1·24	1·17	1·205	2·33
120	4·020	0·1850	0·9703	35·39	1·31	1·27	1·29	2·11

Propionamide (M.W. = 73).

80°	3·796	0·1778	0·9597	31·77	—	—	—	—
90	3·718	0·1779	0·9517	30·88	1·29	1·33	1·31	2·06
105	3·599	0·1779	0·9395	29·50	1·35	1·31	1·33	2·01
120	3·478	0·1779	0·9272	28·14	1·36	1·37	1·365	1·94

Lactamide (M.W. = 89).

80°	4·272	0·1850	1·1381	44·12	—	—	—	—
90	4·226	0·1850	1·1301	43·34	1·06	1·04	1·05	2·87
105	4·152	0·1850	1·1181	42·13	1·12	1·13	1·125	2·59
120	4·076	0·1850	1·1062	40·91	1·13	1·15	1·14	2·54

Benzamide (M.W. = 121).

130°	3·886	0·1850	1·0792	38·06	—	—	—	—
140	3·846	0·1850	1·0717	37·40	1·11	1·08	1·095	2·70
150	3·804	0·1850	1·0641	36·73	1·16	1·26	1·21	2·32
160	3·756	0·1850	1·0565	36·01	1·29	1·25	1·27	2·16
170	3·702	0·1850	1·0489	35·23	1·43	1·43	1·43	1·81

Phenylacetamide (M.W. = 135).

160°	3·644	0·1850	1·0179	33·66	—	—	—	—
170	3·587	0·1850	1·0105	32·89	1·58	1·51	1·545	1·61
180	3·522	0·1850	1·0029	32·05	1·77	1·70	1·735	1·35

Salicylamide (M.W. = 137).

140°	3·785	0·1850	1·1749	40·35	—	—	—	—
150	3·746	0·1850	1·1663	39·64	1·22	1·18	1·20	2·35
160	3·700	0·1850	1·1578	38·87	1·40	1·36	1·38	1·90
170	3·648	0·1850	1·1493	38·04	1·55	1·55	1·55	1·59

Anilides and Urethanes.

Formanilide (M.W. = 121).

60°	3·871	0·1850	1·1115	39·04	—	—	—	—
75	3·790	0·1850	1·0971	37·73	1·49	1·48	1·485	1·69
90	3·700	0·1850	1·0866	36·48	1·55	1·55	1·55	1·60
105	3·599	0·1850	1·0743	35·08	1·75	1·70	1·725	1·36

Acetanilide (M.W. = 135).

120°	3·938	0·1778	1·0261	35·24	—	—	—	—
130	3·868	0·1778	1·0179	34·34	1·86	1·88	1·87	1·21
145	3·762	0·1778	1·0055	32·99	1·87	1·89	1·88	1·20
160	3·652	0·1779	0·9933	31·65	1·88	1·93	1·905	1·17

Anilides and Urethanes (continued).

Methylacetanilide (M.W. = 149).

$t°$.	h.	r.	ρ.	γ.	k_1.	k_2.	k.	x.
105°	3·524	0·1850	1·0036	32·09	—	—	—	—
115	3·448	0·1851	0·9951	31·15	2·14	2·22	2·18	0·96
120	3·406	0·1851	0·9910	30·65	2·22	2·21	2·215	0·94
130	3·330	0·1851	0·9828	29·71	2·24	2·24	2·24	0·92
145	3·206	0·1851	0·9703	28·24	2·33	2·27	2·30	0·88

The ranges of temperature for which the values of k are calculated are:— 105—115°; 105—120°; 115—130°; 130—145°.

Ethylacetanilide (M.W. = 163).

$t°$.	h.	r.	ρ.	γ.	k_1.	k_2.	k.	x.
60°	3·800	0·1850	0·9938	34·27	—	—	—	—
75	3·681	0·1850	0·9798	32·73	2·46	2·46	2·46	0·80
90	3·554	0·1850	0·9657	31·15	2·58	2·49	2·535	0·76
105	3·424	0·1851	0·9516	29·58	2·59	2·60	2·595	0·74

Ethylurethane (M.W. = 89).

$t°$.	h.	r.	ρ.	γ.	k_1.	k_2.	k.	x.
60°	3·314	0·1851	1·0459	31·47	—	—	—	—
75	3·205	0·1851	1·0313	30·01	1·51	1·48	1·495	1·69
90	3·095	0·1851	1·0162	28·56	1·53	1·51	1·52	1·65
105	2·980	0·1851	1·0005	27·07	1·58	1·56	1·57	1·57

Phenylurethane (M.W. = 165).

$t°$.	h.	r.	ρ.	γ.	k_1.	k_2.	k.	x.
60°	3·680	0·1850	1·0792	36·04	—	—	—	—
75	3·576	0·1850	1·0677	34·65	2·18	2·15	2·165	0·97
90	3·468	0·1851	1·0538	33·18	2·25	2·19	2·22	0·93
105	3·354	0·1851	1·0399	31·67	2·39	2·41	2·40	0·83

The following results, which we do not consider it necessary to give in full, have also been obtained. *Acetonitrile*: 20—30°, $k = 1·47$, $x = 1·73$; 30—45°, $k = 1·53$, $x = 1·63$; 45—60°, $k = 1·56$, $x = 1·58$, in good agreement with the values of Dutoit and Friderich (*loc. cit.*) and Renard and Guye (*loc. cit.*). *Propionitrile*: 20—30°, $k = 1·63$, $x = 1·48$; 30—45°, $k = 1·63$, $x = 1·48$; 45—60°, $k = 1·66$, $x = 1·44$, agreeing substantially with the results of Ramsay and Shields and Renard and Guye, but not with those of Dutoit and Friderich. *Aniline*: 20—45°, $k = 1·695$, $x = 1·40$; 45—75°, $k = 2·005$, $x = 1·09$, in agreement with Dutoit and Friderich.

We have also confirmed the abnormal result obtained by Dutoit and Friderich for diphenylamine.

In the case of ethylurethane, we have obtained values which agree well with those of Guye and Baud, but entirely different results with phenylurethane. The authors mentioned found, between 63·8° and 108·8°, $k = 1·38$; and 108·8° and 152·8°, $k = 1·81$, values indicative of pronounced association. In benzene solution, phenylurethane is but slightly associated, much less so than ethylurethane, which, at the lower range, Guye and Baud did not find associated as much as phenylurethane.

The general results are discussed in the sections below.

The Molecular Complexity of the Amines.

Broadly speaking, we may say that the primary amines are slightly associated, the secondary and tertiary amines non-associated in the liquid state. Such other data as exist confirm our conclusions. Thus, Kahlenberg (*J. Physical Chem.*, 1901, **5**, 284), by measurement of Trouton's constant, found that amylamine is somewhat associated, but dipropylamine and di*iso*butylamine are normal. The measurements on aniline in naphthalene solution (Auwers and Pelzer, *loc. cit.*) and our own determinations in solution, quoted below, add further confirmation.

As is the case with other classes of associated substances, the extent of association diminishes with increase in the molecular weight. We deduce from this fact that the parent substance, ammonia, in the liquid state, should show pronounced association, and that the degree of association should be higher than found by Walden (*loc. cit.*, p. 196) (compare Franklin and Kraus, *Amer. Chem. J.*, 1899, **21**, 8; *J. Physical Chem.*, 1907, **11**, 558).

More exact interpretation of the results than is given in the preceding paragraph is somewhat difficult to make. If the primary amines are associated, are the secondary and tertiary amines, with their high values of k, dissociated?

Substances other than the amines are known having values of the Ramsay and Shields' constant higher than 2·12. Walden (*loc. cit.*, p. 212) quotes, from different sources, a number of such substances. Homfray and Guye (*J. Chim. phys.*, 1903, **1**, 518) showed that in a series of esters examined the value of k increased with the complexity of the molecule, until, with pelargonyl malate, $k = 3{\cdot}68$. The alteration in the value of k with constitution is perhaps more simply brought out with the amines than in the case of the esters. In the following summary, the values of k are given for the temperature range (except in the case of tribenzylamine) of 30—45°, and it is evident that in the amines the value increases with (1) the number of hydrogen atoms substituted, (2) the mass of the substituting group:

n-Propylamine	1·84	Benzylamine	2·12
Dipropylamine	2·29	Dibenzylamine	2·85
Tripropylamine	2·635	Tribenzylamine	3·58 (120—135°)
*iso*Amylamine	2·03		
Triamylamine	3·14		

Reference to the anilides will show a similar regularity.

Homfray and Guye suggested that the high values of k obtained by them might be due either to the fact that the molecules were not spherical or to actual dissociation of the molecules, and they found support for the latter view from calculations based on

Longinescu's method (*J. Chim. phys.*, 1903, **1**, 296), and from the cryoscopic observations of Freundler (*Bull. Soc. chim.*, 1895, [iii], **13**, 1055).

Other methods of testing the molecular complexity in the liquid state are, however, not in favour of the idea that dissociation occurs. Walden (*loc. cit.*), using a formula which he had found to be generally valid for non-associated liquids, showed that a number of the substances having high values of the Ramsay and Shields' constant did not differ from the well-recognised normal substances; whilst Kurbatoff and Eliséeff (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1422) have pointed out that the esters examined by Homfray and Guye are normal according to the values of Trouton's constant which they possess.

Evidence of dissociation in the liquid state should be revealed, perhaps to a less extent, in solution, and the dissociation should increase with the concentration. We have, accordingly, determined the molecular weights, in benzene solution, of the amyl- and benzylamines. In the tables, the association factor, $x, = \frac{\text{M.W. (obs.)}}{\text{M.W. (calc.)}}$.

Molecular Weights in Benzene Solution.

iso*Amylamine* (M.W. = 87·1).

Solvent: 15·03 grams.

w (grams).	Δ°.	M.W. (obs.).	x.
0·2916	1·091	88·9	1·022
0·5253	1·753	99·7	1·146
0·9932	3·205	103·1	1·185
1·375	4·395	104·1	1·196

Benzylamine (M.W. = 107·1).

Solvent: 16·06 grams.

0·5562	1·568	110·4	1·03
0·7489	2·055	113·5	1·06
1·348	3·485	122·4	1·14
1·497	3·792	122·9	1·15

Triamylamine (M.W. = 227·3).

Solvent: 14·83 grams.

w (grams).	Δ°.	M.W. (obs.).	x.
0·2912	0·337	219·2	0·97
0·5592	0·833	226·3	1·00
1·035	1·495	233·3	1·03
1·293	1·858	234·7	1·034

Dibenzylamine (M.W. = 197·1).

Solvent: 14·88 grams.

0·1395	0·253	185·3	0·94
0·4995	0·871	192·7	0·98
1·187	2·021	197·3	1·00
1·490	2·536	197·4	1·00

Tribenzylamine (M.W. = 287·2).

Solvent: 15·23 grams.

w (grams).	Δ°.	M.W. (obs.).	x.
0·3406	0·402	278·3	0·97
0·7660	0·926	271·3	0·95
1·173	1·406	273·8	0·95
1·534	1·861	270·7	0·94

Our results afford further evidence that the primary amines are associated, but there is no evidence of any dissociation of triamylamine or dibenzylamine. The results with tribenzylamine are low, but in no way commensurate with the apparent dissociation in the fused state.

As a final test, we plotted the values of molecular surface energy against the temperature for triamylamine, dibenzyl- and tribenzylamine, since Dutoit and Friderich (*loc. cit.*) found that the coefficient of the molecular surface energy of the normal liquids which they examined was independent of the temperature. The following values were used:

Triamylamine, 1060·7; 1029·8; 982·1; 935·0; 887·0.
Dibenzylamine, 1353·0; 1324·0; 1280·2; 1257·7; 1190·5.
Tribenzylamine, 1460·0; 1425·8; 1372·0; 1318·4.

The temperatures are given in the tables (pp. 2073, 2074). In each case, the straight line joining the end-points passed, almost perfectly, through all the points.

We must conclude therefore that the abnormal results under discussion are due to the non-validity of the Ramsay and Shields' formula.

The Nitrosoamines and the Nitriles.

As in the nitro-compounds, so also in the nitroso-compounds here examined, association occurs only in the aliphatic series. The cause of association is to be connected with the nitroso-group, since the secondary and tertiary amines are non-associated.

The tendency of the nitriles to associate is also only marked in the aliphatic series. Benzonitrile has a slight tendency to association, and the property is exhibited distinctly by *m*-toluonitrile. The other aromatic nitriles, save mandelonitrile, which is associated, exhibit abnormally high values of k.

It will not escape notice that the introduction of a hydroxyl group into the substance considerably raises the association, as in lactonitrile and mandelonitrile (see also lactamide).

The Amides.

The amides in the liquid state are very strongly associated, and, unlike the nitriles, nitro- and nitroso-compounds, this association extends to the aromatic as well as to the aliphatic compounds. Indeed, the extent of association in benzamide and salicylamide is striking.

From the following table of association factors, it will be seen that the extent of association is roughly of the same order as that existing in the hydroxyl-containing substances—the organic acids and the alcohols. The data for the acids, alcohols, water, and phenol are taken from the papers of Ramsay and Shields (*loc. cit.*) and Ramsay and Aston (Trans., 1894, **65**, 168). Since data at exactly comparable temperatures are not available, the actual temperatures are quoted:

H_2O	(20—30°)	3·81
$CH_3{\cdot}OH$	(16—46°)	3·43
$C_2H_5{\cdot}OH$	(16—46°)	2·74
$C_3H_7{\cdot}OH$	(16—46°)	2·25
$C_6H_5{\cdot}OH$	(46—78°)	1·43

$H{\cdot}CO_2H$	(16—46°)	3·61
$CH_3{\cdot}CO_2H$	(16—46°)	3·62
$C_2H_5{\cdot}CO_2H$	(16—46°)	1·77

$H{\cdot}CO{\cdot}NH_2$	(20— 30°)	6·18
$CH_3{\cdot}CO{\cdot}NH_2$	(85— 95°)	2·47
$C_2H_5{\cdot}CO{\cdot}NH_2$	(80— 90°)	2·06
$C_6H_5{\cdot}CO{\cdot}NH_2$	(130—140°)	2·70

The outstanding feature of the results recorded is undoubtedly the high associative power exhibited by formamide. Walden (*Zeitsch. physikal. Chem.*, 1906, **54**, 180) expressed the belief that this substance is strongly associated, but made no measurement of its complexity save in aqueous solution, in which it possessed the normal molecular weight. Again (*Proc. Faraday Soc.*, 1910, 156), he states that "formamide appears to reproduce nearly all the valuable qualities of water." Save certain fused salts and sulphuric acid, formamide is more strongly associated than any other liquid yet examined. Its molecular complexity, however, decreases rapidly with rise of temperature. Between 20° and 75°, its complexity drops from 6·18 to 3·34, whilst that of water falls only from 3·44 to 2·9.

We suggested (Proc., 1910, **26**, 128) that the solvent power of formamide for salts is connected with its high molecular complexity. Acetamide has also been found a solvent for salts (Walker and Johnson, Trans., 1905, **88**, 1597; Menschutkin, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1415). Formamide and acetamide can also, like water, produce hydrolysis of antimony trichloride (Bruni and Manuelli, *Zeitsch. Elektrochem.*, 1905, **11**, 554).

Passing to the anilides and urethanes, we note that association is diminished by substitution of hydrogen in the amido-group. The result with acetanilide was unexpected. The measurements of Auwers, of Beckmann, and of Meldrum and Turner, made on solutions of the anilides, show clearly that acetanilide is distinctly more associated than formanilide. Quite a different result is obtained on comparing the two substances in the liquid state.

The question whether the tervalent nitrogen atom is responsible for the association in the amides can, we believe, be regarded as answered in the negative. Methyl- and ethyl-acetanilide are non-associated, as also are secondary and tertiary amines, in all of which a tervalent nitrogen atom is still present. It is also obvious, from the results with methyl- and ethyl-acetanilide, that the oxygen atom does not bring about association (compare Meldrum and Turner, 1910, **97**, 1616), a conclusion in agreement with what is already known concerning esters, acid anhydrides, and ether.

Whatever the properties of chemical combination possessed by the nitrogen or oxygen atom, it appears clear that they cannot be held to be the cause of molecular association, and, in most cases, perhaps in all, association only occurs when these elements are present in distinct electronegative groups.

In the case of the amides, it appears that association is only possible when hydrogen is still present in the amide group. The power of molecular association disappears only when the hydrogen is eliminated from this group. Formamide and acetamide, also, like the hydroxylic substances methyl and ethyl alcohols, ethylene glycol, and glycerol, can combine with salts in the same way as water enters into union as water of crystallisation (Titherley, Trans., 1901, **79**, 413; Walker and Johnson, *loc. cit.*; Menschutkin, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1010; Grün and Bockisch, *Ber.*, 1908, **41**, 3465; Röhler, *Zeitsch. Elektrochem.*, 1910, **16**, 419).

Such facts as these might be used as evidence in favour of the hydroxylic constitution of the amides. But the arguments against this theory are very weighty (Meldrum and Turner, Trans., 1908, **93**, 890), and we have to remember that not only do water and formamide possess like properties, but liquid ammonia, an associated liquid, closely resembles water, can produce hydrolysis (ammonolysis, Franklin, *J. Amer. Chem. Soc.*, 1905, **27**, 820), and, like water, can combine with salts.

It is difficult to locate the exact cause of the association in the amides. The apparent connexion between association and power of producing hydrolysis indicates another method by which the cause of association in the amides might conceivably be tested. If, in water, for example, the hydroxyl group is responsible both for the association produced and also for the hydrolysing power of water, then we might assume that the group in the amides which produces hydrolysis is also the cause of association. Bruni and Manuelli (*loc. cit.*) have found that when antimony trichloride is hydrolysed by formamide or acetamide, the entering group, which is equivalent to one chlorine atom, and therefore to the hydroxyl group, is R·CO·NH. Evidence of the nature of the action, if any, of the anilides and urethanes is desirable in this connexion.

Finally, our results bear out the general connexion between the degree of association and the dielectric constant of a liquid. Quite recently, Walden (*Zeitsch. physikal. Chem.*, 1910, **70**, 569) has pointed out that all substances with high dielectric constants possess certain electronegative groups, as OH, NO_2, CO, CN, NH_2, etc. Such groups we know to be present in those carbon compounds which exhibit association, and we should expect to find the dielectric constant and the degree of association run parallel. In the papers already referred to, Walden has made comparison of the two properties. We quote the following values of the dielectric constant, in connexion with the fresh data brought forward in this communication: Formamide (20°), >84; acetamide (83°), 59·2; dimethylnitrosoamine (20°), 53·3; lactonitrile (20°), 37·7; formanilide (liquid), 20·5; acetanilide (liquid), 19·5; phenylacetonitrile (21·5°), 18·2.

These numbers, and the more extensive comparisons by Walden, show that it is generally true that associated substances have high dielectric constants. The converse is by no means true, although, as may be seen, the substances of highest dielectric constant are those which have the highest association factors.

As regards dimethylnitrosoamine, it is quite possible, bearing in mind the abnormal results obtained with secondary and tertiary amines, that its degree of association is greater than our measurements reveal.

The connexion between the dielectric constant and the degree of association, although at best approximate, leads us, when taken in conjunction with the fact that the elements nitrogen and oxygen with unsaturated valencies do not appear of themselves to cause molecular association, to the conclusion that association in liquids is due to electrical rather than, as supposed by Guye and Baud (*Compt. rend.*, 1901, **132**, 1555), to chemical forces.

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CCXIX.—*The Dynamics of the Decomposition of Persulphuric Acid and its Salts in Aqueous Solution.*

By LEILA GREEN and ORME MASSON.

LEVI AND MIGLIORINI (*Gazzetta*, 1906, **36**, ii, 599) have shown that potassium and sodium persulphates decompose in aqueous solution unimolecularly, and that the action is much accelerated by the addition of acids. Our own experiments confirm both of these results. It is, however, somewhat difficult to reconcile them with one another, for the action itself produces acid sulphate, and can, indeed, be followed throughout its course by the increasing acidity, so that the curve should exhibit the features of an auto-accelerated, rather than those of an unmodified, unimolecular action. The difficulty, however, disappears if the acid sulphate product be assumed to ionise only into metal and HSO_4', and to provide practically no $H^{\cdot}$ ions, or if, in other words, sulphuric acid be regarded as a monobasic acid under the conditions of the experiments. The action may then be formulated by the equation:

$$S_2O_8'' + H_2O = 2HSO_4' + \tfrac{1}{2}O_2,$$

which makes it strictly unimolecular in form. On general grounds the assumption may be objected to, but it does not appear possible to explain without it the behaviour of persulphuric acid and its salts, and it will be shown that one can, by its aid, co-ordinate the various results obtained with the acid, its potassium and sodium salts, its barium salt, and mixtures of these with each other, with other salts, and with acids. One or two unexplained difficulties remain, which will be dealt with in the sequel.

The persulphate solutions employed by us were obtained from solutions of the barium salt, prepared from commercial ammonium persulphate by treatment with excess of barium hydroxide in a vacuum and subsequent neutralisation with dilute sulphuric acid.

The initial strength of each persulphate solution was determined by measuring the final acidity produced by boiling a measured volume, the titrations being carried out with standard sodium hydroxide, using methyl-orange as indicator. Comparative tests were made in some cases by the ferrous sulphate and permanganate method, and also by gravimetric determinations of the metal as sulphate. The results in all cases agreed fairly well, but the acidimetric method was found to be the most accurate, besides having the advantage of rapidity. The progress of the decomposition in each experiment was also followed by acidimetry. In all cases the temperature of the thermostat was 80·0°, which was found to give a convenient rate of action, except in the experiments conducted at 70° and 90° for the purpose of fixing a temperature-coefficient. The solution was always divided at the outset into a number of 5 c.c. samples, and these were heated in closed tubes, according to the method described in a previous research on cyanates (Masson and Masson, *Zeitsch. physikal. Chem.*, 1910, **70**, 290).

The persulphates which we have examined may be divided, for the present purpose, into three classes. The first contains those of sodium, potassium, and ammonium, which are neutral salts convertible into soluble acid sulphates. The magnesium salt properly belongs to this class, but differs somewhat in its behaviour from the other members. The second class contains persulphuric acid itself, which doubles its acidity by conversion into sulphuric acid.

The third class contains barium persulphate, which, originally neutral, produces persulphuric acid and insoluble barium sulphate. The course of the action is quite different in each of these classes, and they therefore require separate consideration.

In the sequel we have thought it desirable to economise space by suppressing most of the numerical details of our work, and have therefore given only the essential results, except where fuller treatment appeared necessary.

Class I.—Neutral Persulphates which form Soluble Acid Sulphates.

These cases conform to the equation for simple unimolecular action:

$$\frac{dx}{dt}=k_1(A-x), \text{ or } k_1=\frac{1}{t_2-t_1}\log_e\frac{A-x_1}{A-x_2},$$

where A is the initial concentration of persulphate, and $A-x$ is its value at any subsequent time, t. To avoid some slight uncertainty due to the time required to raise the tubes to the bath temperature, the time at which the first sample was taken from the bath was selected, rather than the moment of immersion, as t_1. The values of k_1 given in table I are averages calculated in each case from several points in a curve covering nearly the whole course of the action. Separate values in any one experiment were found to agree well. It is evident that k_1 is but slightly dependent on the initial concentration, or even on the nature of the metallic radicle.

In this and subsequent tables, the concentrations are expressed in gram-molecules of persulphate per litre, and the times are measured in minutes:

TABLE I.

Salt.	A.	k_1.
$Na_2S_2O_8$	0·226	0·00541
$Na_2S_2O_8$	0·125	0·00577
$Na_2S_2O_8$	0·127	0·00533
$K_2S_2O_8$	0·108	0·00545
$(NH_4)_2S_2O_8$	0·229	0·0061

The curve for the ammonium salt showed rather more irregularity than the others, and its mean velocity-coefficient was, as shown, perceptibly higher. This is perhaps explained by the formation of traces of nitric acid by oxidation, with consequent acceleration, but the divergence from the normal course is only slight.

Experiments with sodium persulphate solution containing added sodium nitrate (selected as a typical neutral salt of the same metal) have proved that the only effect of such addition is to raise slightly the unimolecular constant. Thus, in a test with 0·1283-sodium persulphate and 0·25-sodium nitrate solution, with twelve experimental points covering a range of 85 per cent. decomposition, k_1 was found to vary irregularly between the extreme values 0·0062 and 0·0068, with a mean value of 0·0065. On the other hand, it will be shown that acids largely accelerate the action, and the special influences of added sulphates will also be dealt with later.

The magnesium salt, in contrast to those of the alkali metals, shows distinctly the effect of auto-acceleration, which, in this case, is probably to be explained by the formation of some non-ionised magnesium sulphate and free hydrogen ions, according to the equation:

$$Mg^{\cdot\cdot} + HSO_4' \rightleftharpoons MgSO_4 + H^{\cdot}.$$

Thus, in an experiment in which the initial concentration of magnesium persulphate was 0·2414, the unimolecular coefficient, calculated in the usual way, was found to increase steadily from about 0·0055 (appreciably equal to that of the sodium or potassium salt) at the start to 0·0066 when the action was half completed, and 0·0092 when less than 10 per cent. remained undecomposed. A similar, but much more pronounced, auto-acceleration will be shown to occur in the case of the barium salt, where the precipitation of the insoluble sulphate necessarily adds hydrogen ions to the solution. But the case of persulphuric acid itself must be discussed first.

Class II.—Persulphuric Acid.

In this case the curves obtained are again of the simple unimolecular form, with no sign of acceleration by increase of hydrogen ions; but it differs in two respects from that of the persulphates of the alkali metals. In the first place, the velocity is considerably greater, and, in the second place, the value of its coefficient is dependent on the initial concentration, so as to vary in different experiments while constant in any one. These facts are in accordance with the hypothesis already put forward, that the action proceeds practically according to the equation:

$$S_2O_8'' + H_2O = 2HSO_4' + \tfrac{1}{2}O_2,$$

and that it is accelerated by the hydrogen ions which are initially present and remain unchanged in concentration. Such a hypothesis leads to the differential equation:

$$\frac{dx}{dt} = (k_2 + kA)(A - x),$$

where $k_2 + kA$ is necessarily a constant (K) in any given experiment, and

$$K = k_2 + kA = \frac{1}{t_2 - t_1}\log_e\frac{A - x_1}{A - x_2}.$$

A simple explanation suggests itself for this accelerative action of hydrogen ions. It may be assumed that, at the dilutions employed, the great bulk of the persulphuric acid is completely ionised into $2H^{\cdot}$ and S_2O_8'', while a small proportion is converted into $H^{\cdot}$ and HS_2O_8'. If this proportion be small enough, the total $H^{\cdot}$ concentration may be taken as constant and equal to $2A$, whilst that of the S_2O_8'' is appreciably equal to $A-x$, and that of the HS_2O_8' itself is therefore proportional to $A(A-x)$. If, further, the HS_2O_8' has a sufficiently high rate of reaction as compared with the S_2O_8'', it will make itself felt in spite of its small concentration, and the total velocity of the action will be the sum of two velocities, $k_2(A-x)$ and $kA(A-x)$, in accordance with the equation already given.

By comparison of experiments with different A values, it is easy to evaluate k_2 and k; and it has been found in this way that $k_2=0{\cdot}010$ and $k=0{\cdot}163$. These figures are illustrated by a comparison of the found and calculated velocity coefficients in table II. The fact that k_2 is nearly twice as great as the k_1 of sodium or potassium persulphate is difficult to explain on any hypothesis, for it implies some influence of the hydrogen ions other than that represented by the term $kA(A-x)$ and independent of their concentration. It is a fact, however, that, whilst $dx/dt=0{\cdot}0055(A-x)$ holds for the sodium and potassium salts, the equation for persulphuric acid is

$$\frac{dx}{dt}=(0{\cdot}010+0{\cdot}163A)(A-x)=K(A-x).$$

TABLE II.

Persulphuric Acid.

A.	K (found).	K (calculated).
0·2566	0·0527	0·0518
0·1251	0·0304	0·0304
0·1237	0·0302	0·0302
0·0923	0·0258	0·0250
0·0644	0·0210	0·0205
0·0416	0·0184	0·0168

The solutions used in the first, third, and fourth of these tests were prepared from barium persulphate by adding the calculated quantity of sulphuric acid, and were filtered from the barium sulphate; while those used in the second, fifth, and sixth were obtained by allowing barium persulphate solution to decompose automatically at 80°, and contained the precipitated sulphate in suspension. These cases will be discussed later.

Persulphuric Acid with Added Nitric Acid.

In this case there is a permanent increase of the hydrogen ions, and, if the initial concentrations of the two acids (both reckoned as dibasic, that is, as $H_2S_2O_8$ and $H_2N_2O_6$) be respectively A and B, the course of the action should be expressed by the equation:

$$\frac{dx}{dt}=\{k_2+k(A+B)\}(A-x),$$

where $k_2+k(A+B)$ appears as a unimolecular constant in any given experiment, and

$$K=k_2+k(A+B)=\frac{1}{t_2-t_1}\log_e\frac{A-x_1}{A-x_2}.$$

This was confirmed by the experiments summarised in table III. The first of these tests was made with an original mixture of persulphuric acid and nitric acid, while the other three were the later parts of experiments, in which barium persulphate, mixed with nitric acid, was allowed to decompose at 80° until there remained only persulphuric acid and nitric acid in solution, and the subsequent decomposition was then studied. These tests will be referred to later. The figures in the last column of the table show the value which K would have if the nitric acid were absent (compare table II), and are given to indicate clearly its effect.

TABLE III.

Persulphuric Acid with Added Nitric Acid.

A.	*B.*	*K* (found).	*K* (calculated).	*K* (original).
0·1248	0·1242	0·0500	0·0506	0·0304
0·0635	0·1845	0·0508	0·0504	0·0204
0·0628	0·1255	0·0414	0·0407	0·0202
0·0630	0·0634	0·0315	0·0306	0·0203

Mixed Persulphuric Acid and Sodium Persulphate.

The theory for such a case may be given on the assumption that the k_1 and k_2 constants are active approximately in proportion to the unchanging relative quantities of $Na^{\cdot}$ and $H^{\cdot}$, and that the latter also contributes its special accelerative effect. Thus, if the initial $H_2S_2O_8$ be A, and the initial $Na_2S_2O_8$ be B, whilst x represents the total S_2O_8 destroyed, A and B will also represent at any time the $(H^{\cdot})_2$ and the $(Na^{\cdot})_2$ respectively, and

$$\frac{dx}{dt}=\{k_2\frac{A}{A+B}+k_1\frac{B}{A+B}+kA\}(A+B-x).$$

In any given experiment therefore a unimolecular constant should be obtained, and

$$K = k_2\frac{A}{A+B} + k_1\frac{B}{A+B} + kA = \frac{1}{t_2 - t_1}\log_e\frac{A+B-x_1}{A+B-x_2}.$$

In one test, in which $A = 0{\cdot}1285$ and $B = 0{\cdot}1234$, a mean value of 0·0276 was found for K in place of the calculated value 0·0288. In another, in which $A = 0{\cdot}0625$ and $B = 0{\cdot}1250$, the found and calculated values were respectively 0·0183 and 0·0172. The agreement is thus fairly satisfactory in both cases.

Persulphuric Acid with Added Sodium Nitrate.

This case is similar to the last, except that, the permanent concentrations of the $(H^{\cdot})_2$ and $(Na^{\cdot})_2$ being respectively A and B, that of the S_2O_8'' at any time is $A - x$ instead of $A + B - x$. The constant is here therefore

$$K = k_2\frac{A}{A+B} + k_1\frac{B}{A+B} + kA = \frac{1}{t_2 - t_1}\log_e\frac{A-x_1}{A-x_2}.$$

In the only test carried out, $A = 0{\cdot}1377$ and $B = 0{\cdot}0625$, giving the calculated value of the constant as 0·0311. The mean experimental value was 0·0325, which is identical with that calculated on the assumption that the sodium nitrate is quite without effect. The difference is in any case too small to be significant, but it may be pointed out that a similar discrepancy was exhibited by the mixture of sodium persulphate and sodium nitrate, indicating that the latter has a small accelerative effect, not included in the theory, which may, in the present case, compensate for the expected small lowering of the K value.

Class III.—Barium Persulphate.

This case differs from the others in the precipitation of the product barium sulphate, and it differs also in the form of the curve in which x is plotted against t; for this, being at first concave towards the x axis, at once points to strong auto-acceleration. The total change affecting the barium salt is represented by the equation:

$$2BaS_2O_8 + H_2O = H_2S_2O_8 + 2BaSO_4 + \tfrac{1}{2}O_2,$$

and it must occur in two steps, namely:

$$(1)\ S_2O_8'' + H_2O = 2HSO_4' + \tfrac{1}{2}O_2,$$
$$(2)\ 2Ba^{\cdot\cdot} + 2HSO_4' = 2BaSO_4 + 2H^{\cdot}.$$

The first of these is a relatively slow action, and the second keeps pace with it. Thus $2Ba^{\cdot\cdot}$ disappear from the solution for one S_2O_8'' destroyed; and if the latter be x, as in previous cases, it is evident that x also represents the persulphuric acid (or acidity) produced, and $A - 2x$ represents the barium persulphate remaining.

This holds until $A-x=x=\frac{1}{2}A$, when the precipitation of the barium is complete, and subsequent action is concerned only with persulphuric acid. The whole action may thus be divided into two consecutive stages, the characters of which are shown in the following summary:

	Total S_2O_8.	BaS_2O_8.	$H_2S_2O_8$.	Form of curve.
First stage	$A-x$	$A-2x$	x	Autocatalytic
Half-way point	$x=\frac{1}{2}A=A-x$	0	$\frac{1}{2}A$	—
Second stage	$A-x$	0	$A-x$	Simple unimolecular

Three of the six experiments with persulphuric acid solutions summarised in table II were, in fact, the second stages of experiments with barium persulphate, which will now be dealt with in greater detail. Comparison of these with the others shows that the presence of precipitated barium sulphate (since there was no other real difference) does not appreciably affect the velocity of persulphate decomposition by any kind of contact catalysis. A similar conclusion may be drawn from the sodium persulphate solutions of table I, one of which (the third) was mixed with the precipitate beforehand in order to test this question. It may therefore be concluded safely that the formation of this product has no such direct effect on the decomposition of barium persulphate itself in the first stage of the action.

In table II, which referred only to persulphuric acid, A and x were given the corresponding significance, and were equal respectively to $\frac{1}{2}A$ and $x-\frac{1}{2}A$, where the symbols are used in reference to the original barium persulphate contents, as in the above summary. But they must now be used in this latter sense, and the equation for the curve, after the complete precipitation of the barium, must be written $dx/dt=(k_2+kA/2)(A-x)$.

Now, since the whole curve is continuous, it is evident that the equation for the first, or autocatalytic, stage must be such as to become identical with that just given at the half-way point, where $x=\frac{1}{2}A$. But it has been shown already that the k_2 of persulphuric acid and the k_1 of sodium or potassium persulphates have very different values, so that it might fairly be expected that the constant (k_3) for barium persulphate should differ from k_2, and perhaps also from k_1. Such proves to be the case, for it can be shown by a graphic method that the initial velocity of the decomposition of the pure barium salt solution, when it is as yet unmixed with persulphuric acid (when $x=0$), approximates to $dx/dt=0{\cdot}0040A$. We thus have $k_3=0{\cdot}0040$, whilst $k_1=0{\cdot}0055$ and $k_2=0{\cdot}010$, and the catalytic constant $k=0{\cdot}163$. It must therefore be assumed that, in any mixture of two of these salts, the appropriate constants will be operative in proportion to the amounts present, and that, consequently, the equation for the first stage of the barium persulphate action is:

$$\frac{dx}{dt}=\left(k_3\frac{A-2x}{A-x}+k_2\frac{x}{A-x}+kx\right)(A-x).$$

This conforms to the requirements, for the contents of the first bracket are equal to k_3 at the starting point, where $x=0$, and to $k_2+kA/2$ at the half-way point, where $x=A/2$. It will be shown, also, that it expresses the whole of the experimental results with considerable accuracy. It is, perhaps, not superfluous to point out that, if hydrogen and barium persulphates had the same velocity constant (if $k_3=k_2$), the equation would be the ordinary one expressing an autocatalysed unimolecular action, for it would then become $dx/dt=(k_2+kx)(A-x)$.

By integration of the above differential equation, we obtain an equation which may be written:

$$k(M+N)=\frac{1}{t}\log_e\frac{M(N+x)}{N(M-x)},$$

where M and N are constants in any given experiment, but vary with the initial concentration, and have the values:

$$M=\sqrt{\left(\frac{A}{2}+\frac{k_2-2k_3}{2k}\right)^2+\frac{k_3}{k}A}+\left(\frac{A}{2}+\frac{k_2-2k_3}{2k}\right)$$

$$N=\sqrt{\left(\frac{A}{2}+\frac{k_2-2k_3}{2k}\right)^2+\frac{k_3}{k}A}-\left(\frac{A}{2}+\frac{k_2-2k_3}{2k}\right).$$

Such an equation is of but little use for theoretical purposes unless M and N can be evaluated by independent measurements of the fundamental constants from which they are derived; but we are able to do this in the present case, having found already k_2 and k from the study of persulphuric acid, and k_3 from the initial velocity of pure barium persulphate solutions. We are thus enabled to compare the results calculated from the integrated equation with those obtained by experiment.

The details of one complete experiment with initially neutral barium persulphate solution are shown in table IV. The values of M and N, given at the head of the table, were calculated from those of A, k, k_2, and k_3; and the theory of the first stage of the action may be tested by the constancy of $\frac{1}{t}\log_{10}\frac{M(N+x)}{N(M-x)}$ at different values of t, and also by its agreement with the calculated value of $0{\cdot}4343k(M+N)$. Also the time is noted (as read from the curve) at which $x=\frac{1}{2}A$, that is, the time of the complete precipitation of the barium sulphate. The simple unimolecular character of the decomposition of the persulphuric acid in the second stage is shown by the practical constancy of the normal logarithmic function, calculated from the observed values of x and t, and the theory of its dependence on A by a comparison of its mean value with that of $k_2 + kA/2$ (compare table II).

TABLE IV.

Barium Persulphate. $A = 0{\cdot}2502$.

First Stage. $M = 0{\cdot}2840$, $N = 0{\cdot}0216$.

t.	x.	$1/t \log_{10}\dfrac{M(N+x)}{N(M-x)}$.
10°	0·0131	0·0226
25	0·0398	0·0208
35	0·0663	0·0207
45	0·0974	0·0205
50	0·1160	0·0206

Mean constant found .... = 0·0210.
Calculated value of $0{\cdot}4343\,k(M+N)$ = 0·0216.

Second Stage, after complete precipitation of Ba at $t = 52{\cdot}5°$.

t.	x.	$1/t - 60 \log_{10}\dfrac{A - 0{\cdot}1558}{A - x}$.
60°	0·1558	—
70	0·1796	0·0126
85	0·2068	0·0135
100	0·2221	0·0132
115	0·2336	0·0137
135	0·2411	0·0135
155	0·2441	0·0125

Mean constant found .... = 0·0132.
Calculated value of $0{\cdot}4343(k_2 + kA/2)$ = 0·0132.

The details of two tests with smaller concentrations of barium persulphate may be given more briefly. In one of these the value of A was 0·1288, whence $0{\cdot}4343k(M+N) = 0{\cdot}0128$ by calculation, and during the first stage of the action (sixty-five minutes) the values found for $\frac{1}{t}\log_{10}\frac{M(N+x)}{N(M-x)}$ ranged from 0·0130 to 0·0134 (mean = 0·0132). During the second stage of the same experiment, the mean unimolecular constant found was 0·0091 in place of the calculated value 0·0089. In the other case, A was 0·0832, whence $0{\cdot}4343k(M+N) = 0{\cdot}0093$, and the constant found during the first stage (seventy minutes) ranged from 0·0103 to 0·0112 (mean, 0·0109), while the calculated and found unimolecular constants of the second stage were 0·0073 and 0·0080. In this case therefore the numerical agreement was not quite so good as in those of the stronger solutions.

It seems worth while to call attention here to a striking contrast between the persulphate case and that of the decomposition of cyanates in aqueous solution, which in some respects is very similar (Masson and Masson, *loc. cit.*). Barium cyanate, which precipitates barium carbonate, gives a simple unimolecular curve, whilst the cyanates of sodium and potassium, which yield soluble ammonium carbonate, give strongly auto-accelerated unimolecular curves. Barium persulphate, which precipitates barium sulphate, gives strongly auto-accelerated unimolecular curves, whilst the persulphates of sodium and potassium, which yield soluble acid sulphates, give simple unimolecular curves. In the former case, it was proved that ammonium carbonate accelerates the action, whilst in the latter case soluble acid sulphates have no such influence, but their hydrogen ions have, when liberated by the precipitation of insoluble sulphate.

Mixed Barium Persulphate and Barium Nitrate.

If the latter be added in quantity equivalent to the former (or more), the barium ions cannot become exhausted by precipitation as barium sulphate so long as persulphate ions remain, and the whole action can be written:

$$BaS_2O_8 + BaN_2O_6 + H_2O = 2BaSO_4 + 2HNO_3 + \tfrac{1}{2}O_2.$$

The action therefore does not divide into two distinct stages as in the case of initially pure barium persulphate, but is marked throughout its course by continuous precipitation and increase of hydrogen ion concentration. Hence the auto-catalytic character must be also continuous, and this is found to be the case.

If A represent the initial concentration of the barium persulphate and B that of the barium nitrate, the composition of the solution at any subsequent time is such that it contains barium and hydrogen persulphates and nitrates with the following concentrations: $S_2O_8'' = A - x$, $(NO_3')_2 = B$, $Ba^{\cdot\cdot} = A + B - 2x$, and $(H^{\cdot})_2 = x$. The total cations or anions (considered as bivalent) are thus always equal to $A + B - x$.

If, as in the case of initially pure barium persulphate, it be assumed that the barium and hydrogen ions are operative in proportion to their relative concentrations, while the latter also produce their special catalytic effect, we have the following differential equation to express the course of the action:

$$\frac{dx}{dt} = \left\{k_3 \frac{A + B - 2x}{A + B - x} + k_2 \frac{x}{A + B - x} + kx\right\}(A - x),$$

which, by integration, gives:

$$k(M + N) = \frac{1}{t}\left\{\frac{N + A + B}{N + A}\log_e \frac{A(N + x)}{N(A - x)} - \frac{M - A - B}{M - A}\log_e \frac{A(M - x)}{M(A - x)}\right\},$$

where M and N are constants in any given experiment, and have the values:

$$M=\sqrt{\left(\frac{A+B}{2}+\frac{k_2-2k_3}{2k}\right)^2+\frac{k_3}{k}(A+B)}+\left(\frac{A+B}{2}+\frac{k_2-2k_3}{2k}\right),$$

$$N=\sqrt{\left(\frac{A+B}{2}+\frac{k_2-2k_3}{2k}\right)^2+\frac{k_3}{k}(A+B)}-\left(\frac{A+B}{2}+\frac{k_2-2k_3}{2k}\right).$$

An obvious simplification of the formula results where, as in the actual experiment (table V), the barium persulphate and nitrate are given the same initial concentration, or $B=A$. The values of M and N given at the head of the table were calculated from that of A and those of k_3, k_2, and k, as already determined. In the third column are given the found values of the constant:

$$K=\frac{1}{t}\left\{\frac{N+2A}{N+A}\log_{10}\frac{A(N+x)}{N(A-x)}-\frac{M-2A}{M-A}\log_{10}\frac{A(M-x)}{M(A-x)}\right\},$$

which may be compared with each other as to constancy and also with the calculated value of $0{\cdot}4343k(M+N)$, given at the end of the table. The agreement is fairly satisfactory.

TABLE V.

Barium Persulphate and Barium Nitrate in Equimolecular Mixture.

$B=A=0{\cdot}1253.\quad M=0{\cdot}2845.\quad N=0{\cdot}0217.$

t.	x.	K.
10°	0·0062	0·0240
20	0·0147	0·0255
30	0·0223	0·0239
45	0·0355	0·0228
60	0·0457	0·0208
70	0·0577	0·0229
75	0·0643	0·0219
90	0·0791	0·0220
105	0·0926	0·0223
120	0·1019	0·0220
135	0·1105	0·0223
160	0·1200	0·0238
195	0·1236	0·0238

Mean value of K found .... = 0·0229.
Calculated value of $0{\cdot}4343k(M+N)$ = 0·0217.

Barium Persulphate with Added Nitric Acid.

Here, as in the case of pure barium persulphate, the action may be expected to divide itself into two stages, since the barium must be totally precipitated when $x=A-x=\frac{1}{2}A$. If B stand for the added nitric acid (reckoned as dibasic) or for the initial $(H^{\cdot})_2$, the quantity of the latter must steadily increase by production of persulphuric acid during the first stage, where its value is $B+x$; but from the middle point onwards through the second stage it must retain the value $B+\frac{1}{2}A$. As in the simple case, the $Ba^{\cdot\cdot}$ must have the value $A-2x$ until this becomes nil at the middle point, whilst the S_2O_8'' must have the value $A-x$ from first to last. The first stage should therefore show an autocatalytic curve merging into the simple unimolecular one of the second stage, and the respective differential equations should be:

$$\text{(I.)}\quad \frac{dx}{dt}=\left\{k_3\frac{A-2x}{A+B-x}+k_2\frac{B+x}{A+B-x}+k(B+x)\right\}(A-x),$$

$$\text{(II.)}\quad \frac{dx}{dt}=\{k_2+k(B+\tfrac{1}{2}A)\}(A-x),$$

which are identical when $x=\frac{1}{2}A$.

These equations, indeed, follow logically from those already confirmed for the case of a mixture of barium persulphate and barium nitrate, for it is obvious that such a mixture, if it initially contains excess of the former ingredient, must, at a certain point in its history, become converted into a solution of barium persulphate and nitric acid, and subsequently into one of persulphuric acid and nitric acid. There are thus three distinct stages in such an action, and it seems an unavoidable conclusion that the theory which is quantitatively applicable to the mixtures of the first stage (table V) and also to those of the third (table III) must apply equally well to those of the second. Nevertheless, it has been found in a series of experiments with barium persulphate and nitric acid in different proportions that the nitric acid produces initially only about half the acceleration indicated in equation I, although it gradually increases its effect as the action proceeds, and attains full value as an accelerator when the barium is completely precipitated, after which equation II holds well. Without further investigation, it does not seem possible to reconcile these observations.

The Influence of Sulphates, Produced or Added.

As already pointed out, sulphuric acid or acid sulphate is a necessary product of the decomposition of persulphuric acid or persulphates of the sodium class of metals, and yet there is in these cases an entire absence of that autocatalysis which is so marked a feature in the case of barium persulphate, where the growing acidity is due to persulphuric acid formed by the precipitation of barium sulphate. The explanation already suggested is that the negative ions produced are in reality HSO_4' (not SO_4''), so that there is no appreciable increase in the concentration of $H^{\cdot}$ ions (the true accelerator) unless the conditions are disturbed by precipitation or, to a smaller extent, by the process mentioned in the case of the magnesium salt. Briefly, the hypothesis is that sulphuric acid acts practically as a monobasic acid in these solutions, while persulphuric acid itself acts as a dibasic one.

The most direct test of this view, apart from the evidence already given in support of it, is obtained by studying the velocity of the decomposition of persulphuric acid and sodium persulphate solutions, to which have been added beforehand known quantities of sulphuric acid, sodium hydrogen sulphate (that is, sodium sulphate and sulphuric acid), or sodium sulphate. According to the hypothesis, the velocity coefficient should not be affected by adding either sodium sulphate or sodium hydrogen sulphate to sodium persulphate; sodium hydrogen sulphate should produce but a slight lowering of the coefficient of persulphuric acid by adding $Na^{\cdot}$ ions to the solution without altering the $H^{\cdot}$ concentration; sodium sulphate should largely reduce this coefficient by converting free $H^{\cdot}$ into $HSO_4{}'$; and added sulphuric acid should accelerate in both cases, but only to the extent due to it as a monobasic acid, or half as much as the equivalent quantity of nitric acid or of persulphuric acid itself. In all cases the numerical results predicted by the hypothesis can be calculated from a knowledge of the fundamental constants already given, namely, $k_1 = 0{\cdot}0055$ for $(Na^{\cdot})_2$, $k_2 = 0{\cdot}010$ for $(H^{\cdot})_2$, and $k = 0{\cdot}163$ for $(H^{\cdot})_2$ acceleration.

The results of the experiments performed confirm these expectations, with one rather notable exception in the case of the addition of sodium sulphate to sodium persulphate. Here the unimolecular constant, although it has at first the normal and expected value of about 0·0055, quickly diminishes until it reaches a steady value, considerably smaller and dependent on the amount of added neutral sulphate. Four tests were made with approximately $\frac{1}{8}$-molar-sodium persulphate, containing respectively 0·060, 0·125, 0·128, and 0·255 molecule of sodium sulphate. In each case the curve showed a similar retardation until about one-fifth of the persulphate was decomposed, and thereafter, and reckoned from this point, a good unimolecular constant was obtained, the respective values being 0·0035, 0·0025, 0·0025, and 0·0020. These results point to some complication, which, as will be shown, is never met with except in the presence of mixed neutral and acid sulphate, and which is perhaps due to a reverse action in which the dissolved oxygen plays a part; for this product is the only substance present whose quantity is initially nil, and tends, on account of its limited solubility, to increase quickly to a maximum.

In all the other cases the curves showed steady unimolecular actions, and the found velocity coefficients agreed fairly well with those calculated in accordance with the hypothesis. Although the agreement is not quantitatively exact, it is noteworthy that the results fully establish the following facts:

(1) Addition of sodium hydrogen sulphate produces no marked acceleration, showing that it does not add $H^\cdot$ ions; (2) addition of sodium sulphate to persulphuric acid produces a large retardation, which points to a suppression of $H^\cdot$ ions; (3) addition of sulphuric acid produces such acceleration as points to the ionisation of about half its hydrogen.

The results are summarised in table VI. In the first column are given the nature and concentration of the persulphate used. In the second, the added sulphate is similarly specified. In the third, under K (found), is given the experimental unimolecular constant, this being, as in previous cases, the mean of several concordant values found over a large range of action. In the fourth column, under K (calculated), is given the value of $k_1\frac{Na^\cdot}{Na^\cdot + H^\cdot} + k_2\frac{H^\cdot}{Na^\cdot + H^\cdot} + k(H^\cdot)_2$, where the ionic symbols refer to the corresponding concentrations after allowance for the conversion of all SO_4 into HSO_4' ions. In the fifth column, under K (original), is given, for comparison, the value the constant would have if the added sulphate produced no effect whatever.

TABLE VI.

The Effects of Added Sulphates.

Persulphate.	Sulphate.	K found.	K calculated.	K original.
0·1285$Na_2S_2O_8$	0·1338$NaHSO_4$	0·0060	0·0055	0·0055
0·1304$Na_2S_2O_8$	0·1332H_2SO_4	0·0161	0·0179	0·0055
0·1273$Na_2S_2O_8$	0·3767H_2SO_4	0·0372	0·0389	0·0055
0·1185$H_2S_2O_8$	0·1250Na_2SO_4	0·0151	0·0160	0·0293
0·1248$H_2S_2O_8$	0·1366$NaHSO_4$	0·0304	0·0288	0·0303
0·1235$H_2S_2O_8$	0·0508H_2SO_4	0·0370	0·0343	0·0301
0·1276$H_2S_2O_8$	0·1194H_2SO_4	0·0421	0·0405	0·0308
0·1285$H_2S_2O_8$	0·1544H_2SO_4	0·0425	0·0435	0·0309

The Effects of Added Alkali.

Levi and Migliorini found that alkalis accelerate the persulphate decomposition, but to a smaller extent than acids. Our experiments, however, with persulphates of the first class do not confirm this. When sodium or potassium persulphate is mixed with the corresponding alkali in equivalent, or greater, amount, a regular unimolecular curve is obtained with a constant which is almost identical with that characteristic of the pure salt solution. It is, indeed, very slightly smaller, which is probably accounted for by the physical effect of the extra dissolved substance, but there is no evidence of positive or negative acceleration by hydroxyl ions. These, of course, become destroyed as the action proceeds, for they necessarily neutralise the acid sulphate product, and any such catalytic effect would thus continuously diminish, and the curve would not be that of a simple unimolecular action. It is noteworthy that the normal sulphate which results from this neutralisation does not produce any such marked retardation as was observed when the same salt was added beforehand to sodium persulphate, so that it may be concluded that the reaction responsible for that complication can occur only in the presence of both normal and acid sulphate, as already mentioned.

The results of four experiments are summarised in table VII. The k_1 values here may be compared with those cited for the pure salts in table I.

TABLE VII.

Effects of Added Alkali.

Persulphate.	Alkali.	k_1 found.
$0·1192Na_2S_2O_8$	0·2192NaOH	0·0051
$0·1185Na_2S_2O_8$	0·2236NaOH	0·0051
$0·1214Na_2S_2O_8$	0·3434NaOH	0·0049
$0·0797K_2S_2O_8$	0·2040KOH	0·0050

The behaviour of barium persulphate when mixed with barium hydroxide is quite different, and is difficult to reconcile with any general theory. The autocatalytic curve of the pure salt solution has been fully explained by the production of persulphuric acid, but here it is evident that neutralisation must occur continuously, and that the precipitation of barium sulphate is accompanied by a progressive diminution of alkali instead of an increase of acidity. Indeed, the course of the action is followed in practice by alkalimetry instead of the usual acidimetry. Now, as it has been proved that hydroxyl ions exert no appreciable catalytic effect in the case of the salts of the alkali metals, it seems inevitable that barium persulphate, when mixed with sufficient barium hydroxide, should give a continuous simple unimolecular curve with its own velocity constant (k_3). Nevertheless, the curves obtained show a much higher initial velocity than corresponds with k_3, that is, an initial acceleration by the added alkali, and they also give evidence of a further acceleration as the alkali subsequently diminishes. We are unable to explain these facts.

The Temperature Effect.

Experiments were made with sodium persulphate and with persulphuric acid at 70° and 90° for comparison with those at 80° already described. The mean values of the unimolecular coefficients are given in the following table. In the case of persulphuric acid, it must be remembered that this coefficient is largely dependent on the initial concentration (A), for it has been shown to be the sum of two terms, $k_2 + kA$, whereas in the case of the salt it is a simple constant, k_1. It appears, however, that the constants at 90° are all about tenfold those at 70°.

TABLE VIII.

The Temperature Effect.

Salt.	A.	Unimolecular coefficients.	Temperature.
$Na_2S_2O_8$	0·125	0·0016	70°
$Na_2S_2O_8$	0·126	0·0055	80
$Na_2S_2O_8$	0·130	0·0161	90
$H_2S_2O_8$	0·124	0·0111	70
$H_2S_2O_8$	0·124	0·0302	80
$H_2S_2O_8$	0·116	0·1035	90

UNIVERSITY OF MELBOURNE.

CCXX.—*A Simple Method of Preparing Tetranitromethane.*

By FREDERICK DANIEL CHATTAWAY.

TETRANITROMETHANE can easily * be obtained without danger, and in almost theoretical amount, by allowing equal molecular amounts of nitric acid † and acetic anhydride to interact ‡ at the ordinary temperature for several days. Some heat is developed on mixing, and slight cooling is necessary during this part of the process, otherwise the action may become so vigorous that loss of material results, but, so far as the author's experience goes, it never becomes explosive in character.

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* The methods hitherto described for the preparation of tetranitromethane, namely, (1) nitrating nitroform (Schischkoff, *Annalen*, 1861, **119**, 247), (2) the action of diacetylorthonitric acid on acetic anhydride (Pictet and Genequand, *Ber.*, 1903, **36**, 2225), (3) distilling nitrobenzene with a large excess of a mixture of nitric and sulphuric acids containing sulphur trioxide (Claessen, D.R.-P. 184229), and (4) adding acetic anhydride to a mixture of nitrogen pentoxide and nitrogen peroxide (Schenck, D.R.-P. 211198, 211199), leave much to be desired in the way of simplicity.

† The use of more than the equivalent amount of nitric acid is of no advantage; indeed, when an excess is added, the yield is seldom so good, as the acid ordinarily employed always contains some small amount of water.

‡ On the 7th of July, since this paper was written, the Farbenfabriken vorm. F. Bayer & Co. published a method (D.R.-P. 224057) of preparing tetranitromethane exactly similar to that given above. As, however, this paper was read about a month earlier, namely, on June 16th (Proc., 1910, **26**, 164), and as many details not to be found in the specification are given, it seems desirable that it should be published in full.

The action takes place almost quantitatively according to the equation:

$$4CH_3{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3 + 4HNO_3 = C(NO_2)_4 + CO_2 + 7CH_3{\cdot}CO_2H.$$

The tetranitromethane remains dissolved in the acetic acid, and separates out as a heavy, oily layer on pouring the product into water. Carbon dioxide is given off almost from the time of mixing, but the evolution is never rapid, and the tetranitromethane appears only to be formed gradually, as the yield is small unless the mixture is kept for some days.

When nitric acid attacks acetic anhydride, a mononitro-derivative is probably first produced, which is nitrated so much more readily than the parent compound that action proceeds until the three hydrogen atoms of a methyl group have been replaced. Hydrolysis then occurs, and the trinitroacetic acid formed slowly decomposes into carbon dioxide and nitroform, which as soon as it is liberated is converted by the remainder of the nitric acid into tetranitromethane.

The operations necessary in this method are so simple and so easily carried out that the preparation is well adapted to take its place in any elementary course of practical organic chemistry to illustrate the ease with which aliphatic compounds can be nitrated, whilst the materials employed are so cheap and the yield is so satisfactory as to make tetranitromethane, which has hitherto been a somewhat unfamiliar substance, one of the most easily procurable of organic compounds.

Preparation of Tetranitromethane.

Thirty-one grams of nitric acid * (D^{15} 1·53) are placed in a 250 c.c. flask, and 50 grams of acetic anhydride are gradually added in quantities of about 2 c.c. at a time, the flask meanwhile being cooled in water, as some little heat is developed. If the flask is not cooled, action proceeds more and more vigorously as the temperature rises, and may, if unchecked, become violent. It is inadvisable therefore to allow the temperature to rise much above 20—25°.

When all the anhydride has been added, the flask is covered loosely by a watch-glass or inverted small beaker, and kept at the ordinary temperature for about a week. As the reaction proceeds, carbon dioxide is continuously but very slowly evolved, and the mixture, which at first is colourless, becomes brown, owing to the formation, in small quantity, of oxides of nitrogen. After a week, the tetranitromethane which remains dissolved in the acetic acid may be separated by pouring the mixture into about 150—200 c.c. of water. The bulk of the tetranitromethane subsides as a colourless, heavy, oily layer, which can be removed by means of a separating funnel, whilst a small quantity still remaining dissolved in the dilute acetic acid may easily be separated by means of a current of steam. The tetranitromethane passes over with the first few c.c. of the distillate, and separates as a heavy globule.

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* The anhydrous nitric acid required in the preparation is most easily obtained by slowly distilling ordinary fuming nitric acid from its own bulk of concentrated sulphuric acid; if ordinary concentrated nitric acid (D 1·41) is used, it is advisable to distil it twice from sulphuric acid. It is not necessary, although advisable if convenient, to distil off the acid under diminished pressure.

The tetranitromethane thus obtained may be freed from traces of acid by washing with water, or even better, although with slight loss, by distilling in a current of steam.* It is then separated and dried over fused calcium chloride.

Tetranitromethane as thus prepared is a heavy, very faintly yellow liquid. It can be distilled at 126° under the ordinary pressure, but the distillate is of a pale brown colour, due to oxides of nitrogen formed by some slight decomposition which takes place at this temperature, and still requires to be washed and dried to obtain it quite pure. If cooled a little below the ordinary temperature, it easily solidifies to a mass of colourless crystals.

The yield of tetranitromethane obtained is never quite the theoretical one, although by careful working it can be made to approximate to it. The small loss cannot be entirely, or even mainly, due to oxidation, as at no period of the action is there any considerable liberation of nitrous fumes; it is probably caused by some of the very heavy vapour being carried away in the escaping carbon dioxide, and lost during the processes of separation.

Using acid prepared as above, without removing the oxides of nitrogen,† the yield is approximately 80 per cent. of the theoretical, about 18—20 grams of pure, dry tetranitromethane being obtained from the weights of materials given.

It is immaterial whether the acetic anhydride be added to the nitric acid, or the nitric acid to the anhydride, but the former procedure is preferable, as the evolution of heat then occurs mainly during the first few additions of anhydride, which can be added more rapidly afterwards.

In a set of experiments to ascertain the rate of formation, a number of similar mixtures of the above quantities were made, and the amount of tetranitromethane formed was estimated after different intervals. After one day, 7·5 grams of tetranitromethane were obtained; after two days, 11·5 grams; after four days, 14·5 grams; after six days, 17 grams; and after eight days, 18·5 grams. After this, further keeping did not appreciably increase the yield.

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* After distilling in a current of steam, the distillate containing the tetranitromethane as well as the residue is always bright yellow in colour, owing to the presence of dissolved nitroform, which is formed in small quantity when tetranitromethane is allowed to come into contact with water or is heated with it.

† There is no great advantage in freeing the anhydrous nitric acid from oxides of nitrogen, as even if the acid is completely colourless on mixing and the mixture is kept at 0° in a dry atmosphere it becomes coloured in a few days. The yield is slightly better if colourless anhydrous acid is employed, but the increased yield does not compensate for the extra labour involved in the preparation of the acid.

The process can be accelerated by heating the mixed liquids cautiously until the action becomes sufficiently rapid to cause the temperature to rise even after removing the source of heat* and then checking the action by cooling; when this has been done several times, the liquid, which at first cannot be heated with safety much above 30°, may be heated to 80—100° without any violent action occurring, but on diluting the product the yield is not found to be anything like so good as when the mixture is simply allowed to remain at the ordinary temperature.

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Oxford.

CCXXI.—*The Constitution of Coumarinic Acid.*

By Arthur Clayton.

When coumarin is dissolved in aqueous sodium hydroxide, the sodium salt of coumarinic acid is produced, whereas the prolonged action of an alcoholic solution of the alkali results in the production of an alkali *o*-coumarate. Coumarinic acid has not yet been isolated, being resolved into coumarin and water at the moment of liberation from its salts, but its alkyl esters are known, these compounds being isomeric with the corresponding derivatives of *o*-coumaric acid. When the dialkyl esters of 3-nitrocoumarinic acid are boiled with aqueous alkalis, 3-nitrocoumarinic acid is produced from the acidified liquid, whereas the dimethyl ester of 3-nitro-*o*-coumaric acid under similar conditions yields the methyl ether of 3-nitro-*o*-coumaric acid (Miller and Kinkelin, *Ber.*, 1889, **22**, 1708 *et seq.*). This difference of behaviour towards alkalis has been explained by Michael's formula (I) for coumarinic acid (*J. pr. Chem.*, 1888, [ii], **38**, 27), which has also received support from Perkin (Trans., 1881, **39**, 560), Miller and Kinkelin (*Ber.*,

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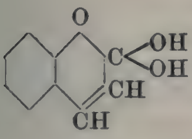
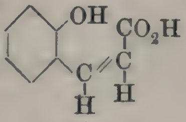
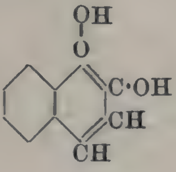
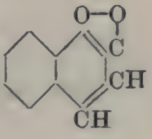
* If the mixture be heated until action becomes violent it is difficult to condens the products, torrents of brown fumes are evolved, and the quantity of tetranitro methane obtained is very small.

1889, **22**, 1713), Roser (*Ber.*, 1882, **15**, 2347), and Anschütz (*Annalen*, 1889, **254**, 181):


(I.)


(II.)


(III).


(IV).

On the other hand, the view has been held that coumarinic acid is the *cis*-isomeride (formula II) of *o*-coumaric acid. A third possible formula (III) is suggested by the constitution which Morgan and Micklethwait (Trans., 1906, **89**, 868) have proposed for coumarin (formula IV).

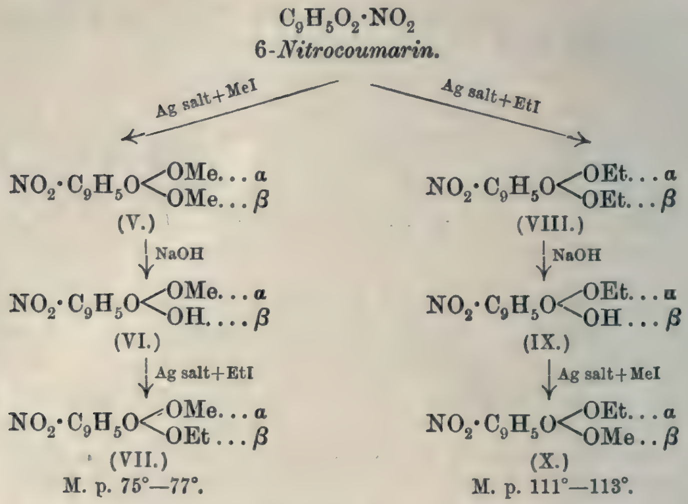
In order to confirm or exclude Michael's formula, the author of the present communication has investigated the alkyl derivatives of 5-nitrocoumarinic acid, the nitro-group being introduced in order to obtain solid compounds. It is obvious that if formula I represents the constitution of coumarinic acid, only one methyl ethyl ester could be prepared, whereas formulæ II and III indicate the possibility of the existence of two such derivatives. For convenience, the two hydroxyl groups will in this paper be distinguished by the letters α and β.

6-Nitrocoumarin dissolves in aqueous alkalis, and the solution, when treated with silver nitrate, yields *silver* 5-*nitrocoumarinate*. This salt, by interaction with methyl iodide, yields *αβ-dimethyl* 5-*nitrocoumarinate* (V). The identity of this substance is established by boiling it with aqueous sodium hydroxide, 6-nitrocoumarin being readily regenerated. The αβ-dimethyl 5-nitrocoumarinate is converted by partial hydrolysis into *α-methyl* 5-*nitrocoumarinate* (VI). The *silver* salt of the latter compound, when treated with ethyl iodide, yields *α-methyl β-ethyl* 5-*nitrocoumarinate* (VII).

By a similar series of operations, *αβ-diethyl* 5-*nitrocoumarinate*, *α-ethyl* 5-*nitrocoumarinate*, and *β-methyl α-ethyl* 5-*nitrocoumarinate* are obtained as indicated by formulæ VIII—X.

All the compounds V—X (p. 2104) are shown to be derivatives of 5-nitrocoumarinic acid by their exceedingly easy reversion to 6-nitrocoumarin when boiled with weak aqueous sodium hydroxide. α-Methyl β-ethyl 5-nitrocoumarinate and β-methyl α-ethyl 5-nitrocoumarinate proved to be distinctly different compounds, the former melting at 75—77°, and the latter at 111—113°, thus showing Michael's formula to be incorrect.

In order that the foregoing proof should not be invalidated by the possibility of one or both of the isomeric methyl ethyl esters


$C_9H_5O_2{\cdot}NO_2$

6-*Nitrocoumarin.*

$NO_2{\cdot}C_9H_5O{<}^{OMe\ldots\alpha}_{OMe\ldots\beta}$ (V.)

$NO_2{\cdot}C_9H_5O{<}^{OMe\ldots\alpha}_{OH\ldots\beta}$ (VI.)

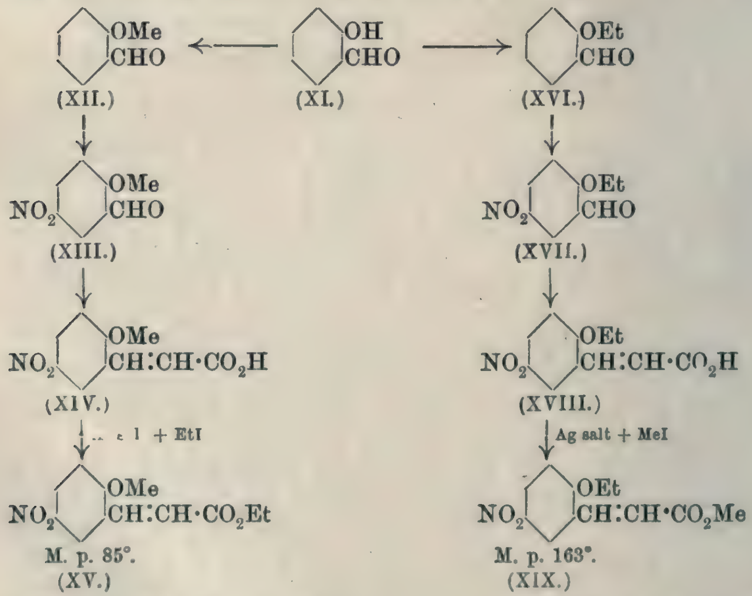
$NO_2{\cdot}C_9H_5O{<}^{OMe\ldots\alpha}_{OEt\ldots\beta}$ (VII.) M. p. 75°—77°.

$NO_2{\cdot}C_9H_5O{<}^{OEt\ldots\alpha}_{OEt\ldots\beta}$ (VIII.)

$NO_2{\cdot}C_9H_5O{<}^{OEt\ldots\alpha}_{OH\ldots\beta}$ (IX.)

$NO_2{\cdot}C_9H_5O{<}^{OEt\ldots\alpha}_{OMe\ldots\beta}$ (X.) M. p. 111°—113°.

being derived from 5-nitrocoumaric acid by the rupture of the lactonic ring, an investigation of the ethers and esters of the latter acid was made as indicated by formulæ XI—XIX.



The methyl ether of 5-nitrocoumaric acid (XIV) was prepared according to Schnell's directions (*Ber.*, 1884, **17**, 1382) as indicated by formulæ XI—XIV, and the *silver* salt of this acid heated with ethyl iodide, thus yielding the *methyl ether* of *ethyl 5-nitro-*

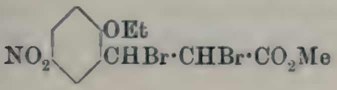
coumarinate (XV). By a similar series of reactions the *ethyl ether* of 5-*nitrosalicylaldehyde*, the *ethyl ether* of 5-*nitrocoumaric acid*, and the *ethyl ether* of *methyl* 5-*nitrocoumarate* are obtained (XVII—XIX).

The two methyl ethyl derivatives of 5-nitrocoumaric acid thus obtained proved to be distinctly different from the methyl ethyl derivatives of 5-nitrocoumarinic acid. The existence of these four isomeric methyl ethyl derivatives permanently excludes the possibility of Michael's formula being correct.

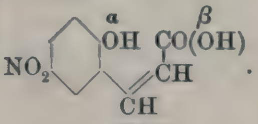
In order to ascertain which of the two remaining formulæ represents the constitution of coumarinic acid, αβ-dimethyl coumarinate and the *methyl ether* of *methyl* 5-*nitrocoumarate* were separately treated with bromine. In each case *methyl αβ-dibromo-5-nitro-2-methoxy-β-phenylpropionate* was produced, thus excluding formula III.

Coumarinic acid is therefore proved to be the *cis*-isomeride of *o*-coumaric acid.

The positions occupied by the hydroxyl groups, which have been distinguished by the letters α and β, are indicated by treating the *ethyl ether* of *methyl* 5-*nitrocoumarate*, and β-methyl α-ethyl 5-nitrocoumarinate separately with bromine. *Methyl αβ-dibromo-5-nitro-2-ethoxy-β-phenylpropionate* (XX) is produced in each case, thus showing that the α-group is phenolic, and that the β-group forms part of the carboxyl group (see formula XXI):

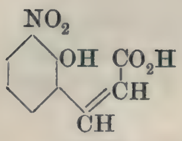


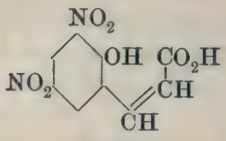
(XX).

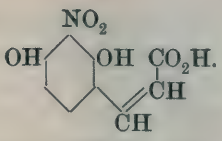


(XXI).

Formula II being established, the chemical behaviour of coumarinic acid can easily be explained. If a representation of the molecule be built up with suitable models, the side-chain is seen to follow approximately the sides of a regular hexagon, and the carboxyl group is brought into close proximity with the phenolic group (formula XXI), thus indicating the ready elimination of the elements of water. If, however, a nitro-group be introduced into position 3, the negative phenolic and nitro-groups exert a combined and powerfully repellent effect on the carboxyl group, which, being repelled from the immediate neighbourhood, no longer enters into chemical action with the phenolic group. This accounts for the fact that 3-nitrocoumarinic acid (XXII), 3: 5-dinitrocoumarinic acid (XXIII), and 3-nitro-4-hydroxycoumarinic acid (XXIV) exist in the free state (Miller and Kinkelin, *Ber.*, 1889, **22**, 1706; Clayton, this vol., p. 1390 *et seq.*):


(XXII).


(XXIII).


(XXIV).

The ease with which the alkyl ether esters of the coumarinic acids undergo complete hydrolysis is unusual, since phenyl ethers are generally not affected by aqueous alkalis. In all probability, however, after the removal of the alkyl from the carboxyl group, two causes operate in the second stage of the hydrolysis, namely, (1), the usual hydrolytic action of aqueous alkalis, and (2), that cause which effects the elimination of the elements of water from coumarinic acid itself. These two influences, acting concurrently, bring about the hydrolysis of the phenyl ether which aqueous alkalis alone are generally unable to effect.

Summary.

1. The two methyl ethyl ether-esters of 5-nitrocoumarinic acid and the two corresponding isomeric ether-esters of 5-nitrocoumaric acid have been prepared.

2. The two methyl ethers of methyl 5-nitrocoumarate and methyl 5-nitrocoumarinate yield the same bromine additive product when treated with bromine.

3. The above facts show that coumarinic acid is the *cis*-isomeride of *o*-coumaric acid. This view of the constitution of coumarinic acid affords a ready explanation of its chemical reactions.

EXPERIMENTAL.

The Ethers and Esters of 5-Nitrocoumarinic Acid.

6-Nitrocoumarin was found to be best prepared by dissolving coumarin in sulphuric acid (10 parts), and treating the solution with one molecular proportion of nitric acid (D 1·4) mixed with three times its volume of sulphuric acid, the temperature being kept below 20°. After one hour the solution is poured on crushed ice, and the precipitated solid crystallised from acetic acid.

Silver 5-nitrocoumarinate was obtained by dissolving 6-*nitro*-coumarin (10 grams) in an aqueous solution of sodium hydroxide (4·2 grams), and then adding a solution of silver nitrate (19 grams). The orange-red precipitate was washed with a little water and dried. When treated with dilute acids, the salt yields 6-nitrocoumarin:

0·2813 gave 0·1908 AgCl. Ag = 51·04.

$C_9H_5O_3N(OAg)_2$ requires Ag = 51·06 per cent.

The Methyl Ether of Methyl 5-*Nitrocoumarinate.*—Silver 5-nitrocoumarinate (6 grams) was mixed with about 30 c.c. of ether, and then shaken with a mixture of methyl iodide (1·5 grams) and ether (10 c.c.) for one hour, the temperature rising during this operation. When cold, the contents were extracted with alcohol, from which solvent colourless needles, melting at 124—125°, were obtained:

0·1375 gave 0·2790 CO_2 and 0·0610 H_2O. C = 55·34; H = 4·92.
0·2146 „ 11·3 c.c. N_2 at 24° and 770 mm. N = 5·99.
$C_{11}H_{11}O_5N$ requires C = 55·70; H = 4·64; N = 5·91 per cent.

The Ethyl Ether of Ethyl 5-*Nitrocoumarinate.*—Silver 5-nitrocoumarinate (10 grams) was treated with ethyl iodide (4 grams) in ethereal solution in the manner described in the preceding experiment, and the product extracted with alcohol. Colourless needles, melting at 104—105°, were obtained:

0·1404 gave 0·3020 CO_2 and 0·0740 H_2O. C = 58·66; H = 5·85.
0·2376 „ 11·7 c.c. N_2 at 25° and 750 mm. N = 5·41.
$C_{13}H_{15}O_5N$ requires C = 58·87; H = 5·66; N = 5·28 per cent.

The Methyl Ether of 5-*Nitrocoumarinic Acid.*—The methyl ether of methyl 5-nitrocoumarinate (6 grams) was dissolved in dilute alcohol, and heated to 100° with aqueous sodium hydroxide (1 gram) for about thirty minutes, when a portion of the liquid produced no turbidity on dilution with water. The mixture was then acidified with dilute hydrochloric acid, and the voluminous precipitate crystallised from alcohol or dilute acetic acid. Colourless needles were obtained, melting at 202—203°:

0·1647 gave 0·3230 CO_2 and 0·0650 H_2O. C = 53·48; H = 4·38.
0·1706 „ 10·1 c.c. N_2 at 26° and 754 mm. N = 6·52.
$C_{10}H_9O_5N$ requires C = 53·81; H = 4·04; N = 6·28 per cent.

The Ethyl Ether of 5-*Nitrocoumarinic Acid.*—This substance was obtained by the interaction of the ethyl ether of ethyl 5-nitrocoumarinate (6·5 grams) and sodium hydroxide (1 gram) in weak alcoholic solution, in the manner described in the preceding experiment. Colourless needles were produced, melting at 171—172°:

0·1498 gave 0·3080 CO_2 and 0·0662 H_2O. C = 56·07; H = 4·94.
0·1442 „ 8·0 c.c. N_2 at 25° and 754 mm. N = 6·14.
$C_{11}H_{11}O_5N$ requires C = 55·70; H = 4·64; N = 5·91 per cent.

The Methyl Ether of Silver 5-*Nitrocoumarinate.*—The methyl ether of 5-nitrocoumarinic acid (10 grams) was dissolved in an aqueous solution of sodium hydroxide (1·8 grams), and the yellow solution treated with aqueous silver nitrate (8 grams), when the silver salt was precipitated as an almost colourless powder:

0·3100 gave 0·1004 Ag. Ag = 32·39.
$C_{10}H_8O_5NAg$ requires Ag = 32·73 per cent.

The Ethyl Ether of Silver 5-Nitrocoumarinate.—The ethyl ether of 5-nitrocoumarinic acid (10 grams) was dissolved in an aqueous solution of sodium hydroxide (1·7 grams). An aqueous solution of silver nitrate (8 grams) was then added. The salt forms an almost colourless powder:

0·3116 gave 0·0980 Ag. Ag = 31·45.

$C_{11}H_{10}O_5NAg$ requires Ag = 31·40 per cent.

The Methyl Ether of Ethyl 5-Nitrocoumarinate.—The methyl ether of silver 5-nitrocoumarinate (10 grams) was heated with ethyl iodide (5 grams) and a little ether for one hour at 100°. The product, when extracted with alcohol, yielded colourless needles, melting at 75—77°:

0·1178 gave 0·2462 CO_2 and 0·0580 H_2O. C = 57·00; H = 5·47.
0·1092 „ 5·7 c.c. N_2 at 24° and 756 mm. N = 5·82.

$C_{12}H_{13}O_5N$ requires C = 57·37; H = 5·18; N = 5·58 per cent.

The Ethyl Ether of Methyl 5-Nitrocoumarinate.—The ethyl ether of silver 5-nitrocoumarinate (10 grams) was mixed with ether and methyl iodide (5 grams), and subjected to the treatment described in the preceding experiment. The alcoholic extract yielded colourless needles, melting at 111—113°:

0·1594 gave 0·3328 CO_2 and 0·0744 H_2O. C = 57·00; H = 5·19.
0·1192 „ 6·4 c.c. N_2 at 24° and 756 mm. N = 5·98.

$C_{12}H_{13}O_5N$ requires C = 57·37; H = 5·18; N = 5·58 per cent.

The Ethers and Esters of 5-Nitrocoumaric Acid.

The Methyl Ether of Silver 5-Nitrocoumarate.—The methyl ether of 5-nitrocoumaric acid (1·6 grams), prepared according to Schnell's directions (*Ber.*, 1884, **17**, 1382), was dissolved in a solution of sodium hydroxide (0·29 gram). To this solution silver nitrate (1·3 grams), dissolved in water, was added, when an almost colourless, gelatinous precipitate was produced:

0·2868 gave 0·0936 Ag. Ag = 32·63.

$C_{10}H_8O_5NAg$ requires Ag = 32·73 per cent.

The Methyl Ether of Ethyl 5-Nitrocoumarate.—The methyl ether of silver 5-nitrocoumarate (1 gram), ethyl iodide (0·5 gram), and a little ether were heated together for three hours at 100°. After evaporating off the ether, the mixture was extracted with alcohol, from which solvent colourless needles, melting at 85°, were obtained:

0·1398 gave 0·2942 CO_2 and 0·0666 H_2O. C = 57·38; H = 5·29.
0·1716 „ 9·0 c.c. N_2 at 25° and 764 mm. N = 5·88.

$C_{12}H_{13}O_5N$ requires C = 57·37; H = 5·18; N = 5·58 per cent.

The Methyl Ether of Methyl 5-Nitrocoumarate.—The methyl ether of silver 5-nitrocoumarate (1 gram) was mixed with methyl iodide

(0·5 gram) and a little ether, and heated to 100° for three hours. After evaporating off the ether, the residue was extracted with alcohol, when colourless needles, melting at 163°, were obtained:

0·1050 gave 0·2150 CO_2 and 0·0454 H_2O. C = 55·84; H = 4·80.
0·1812 ,, 9·9 c.c. N_2 at 764 mm. and 25°. N = 6·07.
$C_{11}H_{11}O_5N$ requires C = 55·70; H = 4·64; N = 5·91 per cent.

5-*Nitro-2-ethoxybenzaldehyde.*—2-Ethoxybenzaldehyde was slowly added to nitric acid (D 1·5), the temperature being kept below 10°. After fifteen minutes the liquid was poured on crushed ice, and the precipitate crystallised from dilute alcohol. The substance crystallises in pale yellow needles, melting at 71—72°:

0·2910 gave 19·3 c.c. N_2 at 25° and 770 mm. N = 7·54.
$C_8H_9O_4N$ requires N = 7·65 per cent.

The Ethyl Ether of 5-*Nitrocoumaric Acid.*—5-Nitro-2-ethoxybenzaldehyde (5 grams), anhydrous sodium acetate (5 grams), and acetic anhydride (15 grams) were boiled together for six hours. The cooled product was ground with water and extracted several times with ether. The ethereal extract was shaken with a solution of sodium carbonate, and the aqueous solution so obtained treated with an excess of hydrochloric acid, when a white precipitate was formed, which crystallised from dilute alcohol in colourless needles, melting at 194—195°:

0·1766 gave 0·3622 CO_2 and 0·0780 H_2O. C = 55·94; H = 4·91.
0·2288 ,, 12·0 c.c. N_2 at 25° and 762 mm. N = 5·87.
$C_{11}H_{11}O_5N$ requires C = 55·70; H = 4·64; N = 5·91 per cent.

The Ethyl Ether of Silver 5-*Nitrocoumarate.*—The ethyl ether of 5-nitrocoumaric acid (10 grams) was dissolved in an aqueous solution of sodium hydroxide (1·7 grams), and a solution of silver nitrate (7·2 grams) then added, when the silver salt was precipitated as an almost colourless, gelatinous mass:

0·3620 gave 0·1132 Ag. Ag = 31·27.
$C_{11}H_{10}O_5NAg$ requires Ag = 31·40 per cent.

The Ethyl Ether of Methyl 5-*Nitrocoumarate.*—The ethyl ether of silver 5-nitrocoumarate (1 gram), methyl iodide (0·5 gram), and a little ether were heated together at 100° for three hours. After evaporating the ether from the product, the residue was extracted with alcohol, from which solvent colourless needles, melting at 141—142°, were obtained:

0·1174 gave 0·2458 CO_2 and 0·0536 H_2O. C = 57·10; H = 5·07.
0·1624 ,, 8·4 c.c. N_2 at 25° and 764 mm. N = 5·80.
$C_{12}H_{13}O_5N$ requires C = 57·37; H = 5·18; N = 5·58 per cent.

The Bromine Additive Products.

Methyl αβ-Dibromo-5-nitro-2-methoxy-β-phenylpropionate.—The methyl ether of methyl 5-nitrocoumarate (1 molecule) was dissolved in carbon disulphide, and treated with bromine (2·5 molecules). After twelve hours the liquid was evaporated, and the residue crystallised from alcohol. Colourless needles, melting at 126°, were obtained. The same product resulted when the methyl ether of methyl 5-nitrocoumarinate was treated in a similar manner:

0·1498 gave 0·1834 CO_2 and 0·0400 H_2O. C = 33·39; H = 2·97.
0·3806 „ 11·5 c.c. N_2 at 25° and 770 mm. N = 3·44.
0·1460 „ 0·1380 AgBr. Br = 40·22.
$C_{11}H_{11}O_5NBr_2$ requires C = 33·25; H = 2·87; N = 3·53; Br = 40·30 per cent.

Methyl αβ-Dibromo-5-nitro-2-ethoxy-β-phenylpropionate.—This compound was prepared from the ethyl ether of methyl 5-nitrocoumarate and bromine by the method described in the preceding experiment, and also by a similar treatment of the ethyl ether of methyl 5-nitrocoumarinate. The substance crystallises from alcohol in colourless needles, melting at 125°:

0·3010 gave 0·2760 AgBr. Br = 39·02.
0·4020 „ 12·5 c.c. N_2 at 25° and 770 mm. N = 3·53.
$C_{12}H_{13}O_5NBr_2$ requires N = 3·41; Br = 38·93.

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant which has in part defrayed the expense incurred during this research.

ROYAL COLLEGE OF SCIENCE, LONDON.
SOUTH KENSINGTON, S.W.

CCXXII.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XVI.* The Relationship between the Chemical Constitution and the Influence of a Solvent.*

By THOMAS STEWART PATTERSON and ELIZABETH FINDLAY STEVENSON, M.A., B.Sc., Robert Donaldson Scholar of Glasgow University.

THE results which have been presented in former papers have made it clear that the rotation of ethyl tartrate, and doubtless also of many other active substances, responds in a remarkable manner to differences in the constitution of the solvents in which the active compound may be dissolved. Thus, in $p=5$ solution in benzaldehyde, ethyl tartrate has a specific rotation of about $+45°$ (Trans., 1909, **95**, 322), whilst in benz*anti*aldoxime at about the same concentration its specific rotation is approximately $-12°$, a difference of 57°. Not only can actual differences of composition produce such variations in rotation, but even the subtle difference of constitution in the *syn-* and *anti*-oximes can readily be detected in this way, whilst other methods of investigation, absorption spectroscopy, for example (Hartley and Dobbie, Trans., 1900, **77**, 509), fail to indicate any dissimilarity.

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* Part XV., Trans., 1909, 95, 1128.

It seems therefore possible that when a sufficient amount of orienting work has been done, an examination of the solvent effect of a given substance on the rotation of ethyl tartrate or other suitable active compound may throw valuable light on the constitution of the substance in question.

In our opinion the mechanism of this process is of a secondary character;* that is to say, the arrangement and relationship of the atoms of the solvent molecules produce a liquid which, in the mass, has at play within it certain characteristic forces, and an active compound dissolved in this liquid, coming under the influence of these forces, has its configuration and consequently its rotation altered as the result. The change of rotation is thus only an indirect effect of the chemical constitution of the solvent. In the first paper of this series the suggestion was made (Trans., 1901, **79**, 188) that the proximate cause of solvent influence on rotation was that property of liquids known as internal pressure, and that variation of internal pressure from solvent to solvent might be indicated by variation of the solution-volume of the dissolved substance. It was also suggested that, since in solutions of finite concentration the total volume change is doubtless shared in by both constituents of the solution, it might be possible to correlate with rotation values, values of molecular solution-volume calculated for infinite dilution, the assumption being made, as a first approximation, that in very dilute solution the change of volume due to solution might be ascribed entirely to the solute. It is clear to us now, however, that this is an untenable assumption, although, of course, in some cases it may closely represent the truth, and thus account for certain regularities which were observed; in general, it could only be substantiated by a strict correspondence between experiment and theory, a correspondence which does not exist. A definite decision as to the existence of a relationship between rotation and solution-volume must be deferred until some method has been found of determining the true volume of the different constituents of a solution.

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* As an instance of a primary effect we may cite absorption spectra. If it be the case, as seems generally to be held, that absorption bands are caused by vibrations inside the molecule which absorb light energy, then such an effect would be of a primary character, since it is directly transmitted to the medium in which it is observed. In regard to a primary effect, no two chemical compounds are likely to be absolutely identical, in much the same way that no two elements appear to have spectral lines in common, but substances of analogous composition will probably produce closely similar effects. On the other hand, however, two substances entirely dissimilar might quite well produce exactly the same secondary effect, just as a given strength of pull might be exerted either by a spring or by a system of gyrostats, that is, in two very different ways. The boiling point of a liquid is a constitutive property of, at least, the second order, so that the same boiling point may be common to liquids having no chemical similarity. The melting point of a compound is a constitutive property of a higher order than the second. It is easy to see that the higher the order the more difficult it will be to interpret the effect, and this accounts for the striking failure to deduce any relationship between the simplest of physical properties, like boiling point, and especially melting point, and chemical constitution.

Some papers have recently appeared in which questions regarding internal pressure are discussed. Winther, in a number of valuable papers (*Zeitsch. physikal. Chem.*, 1907, **60**, 594, 651, 685), has attempted to carry the relationship between rotation and internal pressure much further than Patterson. Dawson (this vol., p. 1041) draws the conclusion that there is no connexion between internal pressure and solution-volume, but that, nevertheless, internal pressure and rotation may be correlative. His experiments point, he considers, to the existence in solutions of compound molecules of solvent and solute. On the other hand, Scheuer (*Zeitsch. physikal. Chem.*, 1910, **72**, 513), setting out with the view that the existence of such compounds is highly probable, was unable to find any evidence of their formation after a very complete and interesting examination of the melting-point curves, the volume relationships, the viscosity, the rotation, and the dispersion of mixtures of diethyl diacetyltartrate and of menthol with various inactive solvents. Amongst other less probable hypotheses, Scheuer therefore also suggests, like Patterson and Winther, that rotation changes on solution may be due to variation of internal pressure from solvent to solvent. It may be added that Grossmann (*Zeitsch. physikal. Chem.*, 1910, **73**, 148), using light of various wave-lengths, has examined the rotation of ethyl tartrate in a number of solvents, almost all of which had already been investigated by Patterson for yellow light. Grossmann is of opinion that his and other experiments render extremely probable the existence of compound molecules of solute and solvent, but no effort whatever is made to show how this conception would explain the results obtained.

Other attempts to establish the existence of compound molecules of solvent and solute in solutions have been no more successful. Armstrong and his students have attacked the problem in various ingenious ways (*Proc. Roy. Soc.*, 1906, *A*, **78**, 272; 1907, *A*, **79**, 564, etc.), as has also Philip (Trans., 1907, **91**, 711), but further investigation by Usher (this vol., p. 66), and in a less degree by Findlay and Creighton (this vol., p. 536), has shown, at least, that the assumptions made in the particular method of attack are unwarranted.

In the absence of satisfactory proof of either view, it appears to us that the purely physical conception has the advantage of simplicity, and ought in the meantime to be adopted. In seeking, therefore, to correlate the chemical constitution of a given substance with its solvent influence, it should be carefully borne in mind that solvent influence being probably at least of a secondary character, any attempt to interpret it ought to be made with particular care.

In a recent paper of the present series (Trans., 1908, **93**, 1838), a commencement was made in the direction indicated, when it was shown by one of us that the solvent influence, on the rotation of ethyl tartrate, of disubstituted benzenes appeared to be governed by the general law that two substituting groups, similar or dissimilar, when in the ortho-position cause the greatest, and when in the para-position the least, rotation in the dissolved active ester. This behaviour was observed in regard to (1) *o*-, *m*-, and *p*-xylene; (2) *o*-, *m*-, and *p*-nitrotoluene; (3) *o*- and *m*-dinitrobenzene; (4) *α*- and *β*-nitronaphthalene; (5) 2 : 6- and 2 : 4-dinitrotoluene.

We have now examined, more or less completely, according to circumstances, the following solvents: phenol, anisole, phenetole, diphenyl ether; *o*-nitrophenol, *o*-nitroanisole, *o*-nitrophenetole; *m*-nitrophenol; *p*-nitrophenol, *p*-nitroanisole, *p*-nitrophenetole; catechol, resorcinol, quinol; pyrogallol, phloroglucinol; *α*-naphthol, *β*-naphthol; *p*-benzoquinone; and also *o*-, *m*-, and *p*-chloronitrobenzene.

A considerable number of these solvents are solids, in some cases of moderately high melting point, and it was therefore occasionally impossible either to examine dilute * solutions at all, or to examine even fairly concentrated solutions satisfactorily at a low temperature, which renders it difficult to institute wide comparisons between the data obtained for different solvents. So far as possible, however, we have extrapolated from our data to 20°, a standard temperature adopted in previous communications, even although many of the solutions could not possibly be examined in the polarimeter at that temperature, and in spite of the fact that the requisite extrapolation entails some loss of accuracy. In other cases comparison has been made at such temperatures as seemed most convenient.

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* With reference to ethyl tartrate.

Of the solvents mentioned above, but little need be said regarding the three last, and we may therefore commence with them. Only one solution in each, of approximately $p=25$, was made up and examined in the polarimeter at several different temperatures. As in this case it is only the relative effect of the *o*-, *m*-, and *p*-positions that comes in question, it is unnecessary to extrapolate to 20°; numbers are given below for the interpolated temperature 90°.

Ethyl Tartrate in o-, m-, *and* p-*Chloronitrobenzene.*

Solvent.	M. p.	p.	$\alpha_D^{90^\circ}$ (100 mm.).	$R_D^{90^\circ}$.*
o-Chloronitrobenzene	32·5°	25·733	+7·26	+28·2°
m-Chloronitrobenzene.........	44·4	28·43	6·19	21·8
p-Chloronitrobenzene	83·0	24·26	3·8	15·7

* $R_D=100\ \alpha_D/p$; it does not differ much from specific rotation.

It is clear that in this set of compounds, also, as in the others already mentioned, the presence of the two substituents in the *o*-position brings about a much more powerful solvent influence than in either of the other two positions.

A general idea of the behaviour of most of the remaining solvents examined will be obtained from the diagram, which represents the effect of diluting ethyl tartrate with the various inactive compounds mentioned at a temperature of 20°, subject to the limitations referred to above.

Phenol (m. p. 42·5°).—Solution in phenol very greatly modifies the specific rotation of ethyl tartrate. The value rises from +7·8° in the pure ester to +48·5° at infinite dilution in phenol, an increase of 40·8°. Since benzene itself has but little effect (Trans., 1902, **81**, 1098), it is clear that the introduction of the hydroxyl group must profoundly modify the interatomic forces of the molecule.

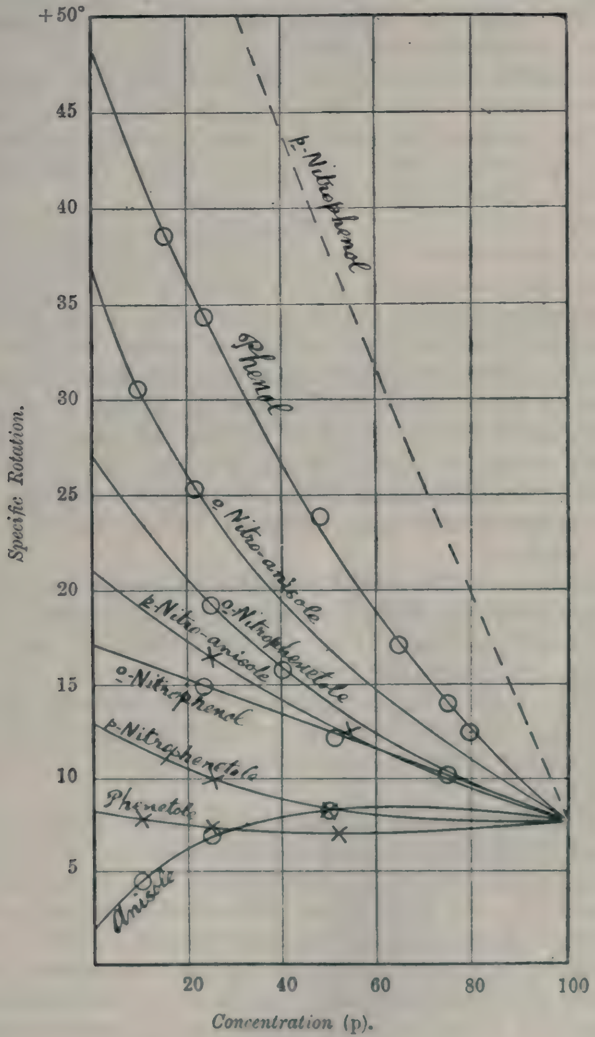
Anisole.—The replacement of the hydroxylic hydrogen by a methyl group brings with it a very great change in solvent influence. The specific rotation of the ethyl tartrate drops to +6·8° in a $p=25$ solution, that is, to a somewhat lower value than in the homogeneous ester. It will be noticed, too, that the shape of the concentration-rotation curve is of the opposite type to that of phenol, being concave to the point of origin of the diagram, in such a way that, starting from the value for the pure ester, the rotation increases slightly on dilution with anisole to reach a maximum value of about +8·2° between $p=50$ and 60, and then diminishes again fairly rapidly to about +2·5° at infinite dilution.

Phenetole.—In comparison with the difference between phenol and anisole, that between anisole and phenetole is slight. For

$p = 25$ solutions the rotation values are much alike (anisole, +6·8°; phenetole, +7·32°), but it will be noticed that in regard to the form of the concentration-rotation curve these two solvents differ, and at infinite dilution the values for the rotation of the dissolved ester are much more divergent (+2·5° and +7·3° respectively).

FIG. 1.

Concentration-rotation curves for ethyl tartrate in various solvents.



The curve for phenetole is of the same type as that for phenol; there is a minimum rotation of +7° at $p=50$, after which the rotation rises to reach the value +8° at infinite dilution.

Diphenyl Ether (m. p. 28°).—Only one solution was examined in diphenyl ether, of $p=24{\cdot}58$. Its observed rotation at 20° was 1·95°, which, assuming a density of unity, gives a specific rotation of +7·93°, about one degree higher than that in anisole and phenetole at the same temperature and concentration.

These results seem to make clear the fact that the powerful influence of phenol in this direction is to be attributed neither to the oxygen atom of the molecule nor to the phenyl group or—in the case of diphenyl ether—groups, but rather to the presence of the hydrogen atom of the hydroxyl group.

o-*Nitrophenol* (m. p. 45°).—Since an *o*-nitro-group in toluene and other monosubstituted benzenes produces a much greater increase of solvent influence than a *m*- or a *p*-nitro-group, we had expected that *o*-nitrophenol would have a greater influence than phenol. On the contrary, however, the rotation at infinite dilution (+17°), although considerably higher than that of homogeneous ethyl tartrate, is much below the rotation in phenol. The effect of *o*-nitrophenol in this respect is in no way the mean of the effects of nitrobenzene and phenol, which are both above +40°. The influence of the substituents is thus certainly not additive.

The concentration-rotation curve for *o*-nitrophenol is a straight line or nearly so.

o-*Nitroanisole*.—The exchange of the hydroxylic hydrogen atom of *o*-nitrophenol for a methyl group brings about, at infinite dilution, a considerable increase—19·5°—in the rotation of the dissolved ester, namely, from +17° to +36·5°.

o-*Nitrophenetole*.—In *o*-nitrophenetole the concentration-rotation curve is very similar to that for the corresponding methyl ether, but lies wholly below it. At infinite dilution the rotation would be +27°.

There is thus between phenol and its ethers, on the one hand, and *o*-nitrophenol and its ethers on the other, a relationship of an inverse character when the solvent effects at infinite dilution are considered. In the former, the high rotation brought about by phenol gives place to a low rotation in anisole, and rises again somewhat in phenetole, whilst in the latter compounds the comparatively low value in *o*-nitrophenol rises to a fairly high value in *o*-nitroanisole, to fall again considerably in *o*-nitrophenetole.

p-*Nitrophenol* (m. p. 114°).—Owing to the higher melting points of the para-derivatives of phenol, observations could not be made, in this series, in so complete a fashion as in others, but sufficient data have been obtained to elucidate the general behaviour of the compounds concerned. In *p*-nitrophenol, two solutions were examined in regard to rotation, density determinations, however, being omitted. In a solution of $p = 47{\cdot}86$ by interpolation from the observed data, $R_D^{100°} = 34{\cdot}6°$,* whilst for $p = 24{\cdot}98$, $R_D^{100°} = 46°$, whence at infinite dilution, also for 100°, the value of R_D would be approximately $= 60°$. These are very high values, and they increase as the temperature falls, so that at 20° the specific rotation, which in this case would have a slightly lower value than R_D, of an infinitely dilute solution of ethyl tartrate in *p*-nitrophenol would probably lie at about $+75°$. *p*-Nitrophenol is thus considerably more powerful even than *α*-nitronaphthalene or *o*-dinitrobenzene, the most powerful of the solvents hitherto examined. But owing to the extensive extrapolation requisite in this case, the concentration-rotation curve for *p*-nitrophenol can only be regarded as a somewhat rough approximation, for which reason it is shown as a broken line in the diagram.

p-*Nitroanisole* (m. p. 54°).—This solvent on mixture with ethyl tartrate causes a gradual and comparatively slight increase of specific rotation. For a solution of $p = 53{\cdot}84$, $[\alpha]_D^{20} = +12{\cdot}5°$. By extrapolation of the observed readings for a $p = 26{\cdot}08$ solution, the value α_D^{20} (100 mm.) $= +5{\cdot}1°$ is found. Assuming a density of 1·2, which would certainly not be far from the truth, the specific rotation at infinite dilution would have a value of, approximately, $+21°$.

p-*Nitrophenetole* (m. p. 60°).—Solutions of $p = 49{\cdot}66$ and $p = 24{\cdot}37$ were examined in this solvent. The specific rotations of these at 20°, assuming a density of 1·2 in each case, would be nearly $+8°$ and $+10°$. With increasing dilution, therefore, the rotation of the dissolved ethyl tartrate increases, although only slowly, to reach a value of about $+13°$ at infinite dilution.

m-*Nitrophenol* (m. p. 96°).—Only one solution—$p = 49{\cdot}76$—was examined. Its behaviour is referred to below.

2 : 4-*Dinitrophenol* (m. p. 114·5°).—We also examined one solution ($p = 75{\cdot}15$) in this substance. Its rotation was somewhat lower than that of an equally concentrated solution in *o*-nitrophenol.

General Discussion of the Foregoing Results.

1. We may examine first the solvent influence of phenol and its three nitro-derivatives, which will be best accomplished by considering the observed rotations for $p = 50$ solutions at a temperature of 70°:

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* See note on p. 2113.

Solvent.	p.	$\alpha_D^{70°}$ (100 mm.).	Difference.
o-Nitrophenol	51·13	+ 9·3°	
			2·5°
Phenol	48·2	11·8	
			3·5
m-Nitrophenol	49·76	15·3	
			2·4
p-Nitrophenol	47·86	17·7	

The influence of phenol is diminished 2·5° by the introduction of a nitro-group in the *o*-position; it is raised 3·5° by a nitro-group in the *m*-position and by a further 2·4° if the nitro-group be in the *p*-position, a behaviour which is thus just the opposite of that observed in other cases of ortho-, meta-, and para-isomerism.

2. Comparing the behaviour of phenol, *o*-nitrophenol, and *p*-nitrophenol with that of their respective ethers, it is to be noticed that the very great solvent influence of phenol disappears almost entirely in anisole, phenetole, and diphenyl ether, and that in a similar manner the very powerful effect of *p*-nitrophenol is greatly diminished in its methyl and ethyl ethers, and by an approximately equal amount in the two cases, some 50°. On the contrary, however, the comparatively feeble effect of *o*-nitrophenol is quite considerably raised in its ethers. Thus phenol and *p*-nitrophenol appear to behave in an analogous manner, and to differ from *o*-nitrophenol, as is shown in the table below.

Rotation of Ethyl Tartrate.

Solvent.	$[\alpha]_D^{20°}$ Infinite dilution.	Difference.	Solvent.	$[\alpha]_D^{20°}$ Infinite dilution.	Difference.	Solvent.	$[\alpha]_D^{20}$ Infinite dilution.	Difference.
Phenol	+48·5°	+46°	p-Nitrophenol	+75°	+54°	o-Nitrophenol	+17°	- 19·8°
Anisole	+ 2·5		p-Nitroanisole	+21		o-Nitroanisole	+36·8	

3. As shown in the following table, *o*-nitroanisole has a greater solvent influence than *p*-nitroanisole, and *o*-nitrophenetole a greater effect than *p*-nitrophenetole, and by almost the same amount.

Rotation of Ethyl Tartrate.

Solvent.	$[\alpha]_D^{20°}$ Infinite dilution.	Difference.	Solvent.	$[\alpha]_D^{20°}$ Infinite Dilution.	Difference.
o-Nitroanisole ...	+36·8°	15·8°	o-Nitrophenetole ...	+27°	14°
p-Nitroanisole ...	21·0		p-Nitrophenetole ...	13	

Although, therefore, the behaviour of the nitrophenols is unusual, inasmuch as the two substituting groups produce the greatest solvent effect when in the *p*-position, and least when in the *o*-position, this exceptional behaviour does not extend to their ethers, which exhibit the regularity previously described for the chloronitrobenzenes and a number of other substances.

4. It is of interest to compare, so far as is possible, our present results with some obtained by other methods having a similar aim. E. C. C. Baly and Miss Ewbank (Trans., 1905, **87**, 1315) have described the absorption curves for phenol, anisole, and phenetole. They point out that the curves for the ethers are identical, and that they differ in one particular * from that of phenol itself. This agrees roughly with what we have found, for, although the concentration-rotation curves for anisole, phenetole, and diphenyl ether are certainly not identical, still, in respect to the magnitude of their effect when compared with phenol, they are much alike. That for phenol differs very markedly.

We had also, during the course of this research, compared our results with the absorption curves given by Baly, Edwards, and Stewart (Trans., 1906, **89**, 512) for the nitrophenols and their ethers, but in a more recent paper Baly, Tuck and Marsden (this vol., p. 571) have explained the anomalous character of one earlier experimental result † as being due to solvent influence, and have considerably altered the theoretical views formerly held. They have rejected the idea of the existence of a quinonoid structure, not only in the free nitrophenols, but also in their alkali salts, and they draw the conclusion that *o*-nitrophenol and *o*-nitroanisole are similarly constituted, the same holding for the meta- and para-compounds.

It may be pointed out that our results, if it be legitimate to compare them with those of Baly, are not in agreement with this conclusion, since, as stated above, phenol and *p*-nitrophenol are related to their ethers in a similar manner, the solvent influence of the phenols being much greater than that of the ethers, whereas the opposite is the case for *o*-nitrophenol and its ethers. The ethers of phenol, *o*-nitrophenol, and *p*-nitrophenol, however, behave normally amongst themselves. It might therefore be concluded that phenol and *p*-nitrophenol are similar in structure and different from *o*-nitrophenol, but that the ethers are all of analogous constitution.

The data which we have obtained in the examination of a number of polyhydroxy-benzenes and of *p*-benzoquinone may be dealt with very briefly. In the table below, there are quoted interpolated values for the observed rotation at 100° of solutions all of about the same concentration.

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* We are not aware what degree of importance Professor Baly would attribute to this difference.

† That the spectrum of *o*-nitroanisole differed from that of *o*-nitrophenol.

Rotation of Ethyl Tartrate.

Solvent.	*p.*	$a_D^{100°}$ (100 mm.).
Benzene	75·199	+10·9°*
Phenol	74·39	13·82
Catechol	74·81	13·45
Resorcinol	74·10	16·55
Quinol	74·47	17·60
Pyrogallol	74·93	13·25
Phloroglucinol	74·33	17·20
p-Benzoquinone	74·98	10·90

* By extrapolation from figures given in Trans., 1902, **81**, 116.

On account of the rather high melting points of these substances, only one concentrated solution in each was examined.

Catechol, *Resorcinol*, *Quinol*.—The first hydroxyl group introduced into the benzene ring produces a considerable increase of solvent influence. A second, however, in the *o*-position to the first, instead of causing a further increase, brings about a slight diminution of less than half a degree. In the *m*-position, on the other hand, an increase of nearly three degrees results, whilst in the *p*-position the increase is almost four degrees.

Pyrogallol, *Phloroglucinol*.—The behaviour of these two solvents is in remarkably close accordance with what might now be expected. The three hydroxyl groups in the vicinal position in pyrogallol bring about a small diminution as compared with catechol, whilst in the *m*-position in phloroglucinol there is a considerable increase as compared with resorcinol. It is thus quite clear that two hydroxyl groups have least effect in the *o*-position and most in the *p*-position, a behaviour which is thus similar to that shown by a nitro-group and a hydroxyl group when present together in the benzene ring, but opposite to that which is characteristic of two nitro-groups, two methyl groups, or a methyl group and a nitro-group.

p-*Benzoquinone* (m. p. 166°).—*p*-Benzoquinone, in a solution of approximately the same strength as for the polyhydroxy-benzenes, caused for $a_D^{100°}$ the value +10·9°, a considerably lower rotation than is produced by phenol or catechol. It might therefore be argued that a quinonoid structure of the solvent causes, in ethyl tartrate, a lower rotation than a simple phenolic constitution, and that therefore the low rotation produced by *o*-nitrophenol as compared with phenol and *p*-nitrophenol may be due to a quinonoid structure for the *o*-nitrophenol. We would not venture, of course, on this slight evidence, to draw any definite conclusion, but the fact is worthy of consideration along with others bearing on the question.

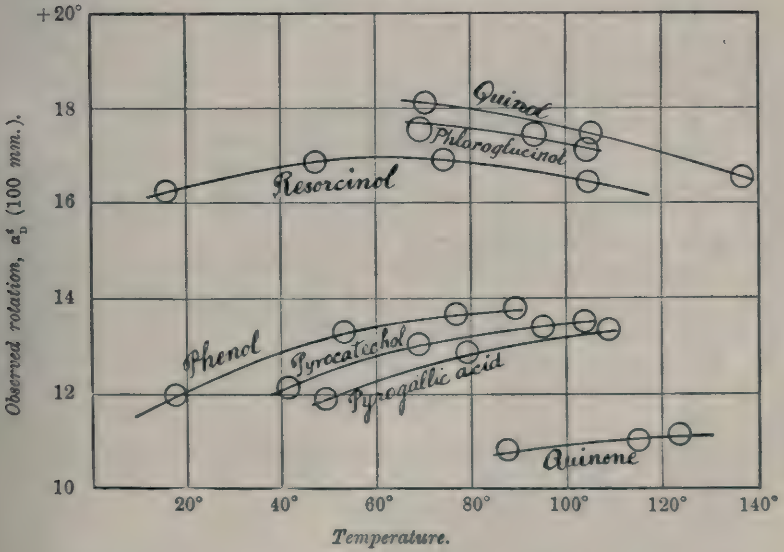
α- and β-Naphthol (m. p. 94° and 122°).—We also examined one solution each in α- and β-naphthol. In the former, $R_{\mathrm{D}}^{100^\circ}$ ($p = 25\cdot24$) = $+29\cdot7^\circ$, and in the latter, $R_{\mathrm{D}}^{100^\circ}$ ($p = 29\cdot01$) = $+43\cdot8^\circ$. The difference is thus very considerable, and since the α-compound may be regarded as an *o*-hydroxy- and the β-compound as a *m*-hydroxy-derivative of benzene, the behaviour of these two solvents is strictly in accordance with that of the other phenols dealt with above.

Influence of Change of Temperature.

With regard to the influence of change of temperature on the rotation of these solutions, but little need be said, since the behaviour observed has been entirely in agreement with what has been discovered in other cases. The effect of rise or fall of temperature is a function of the value of the rotation at the temperature chosen. If the rotation at T° be above a certain critical value for that temperature, a value which can be fairly definitely stated,* then heating above T° will cause fall of rotation, whereas if the rotation be below the critical value, further heating will bring about increase of rotation. The temperature-rotation curves in Fig. 2 illustrate

FIG. 2.

Temperature-rotation curves for ethyl tartrate in various solvents (p = approximately 75 in each case).



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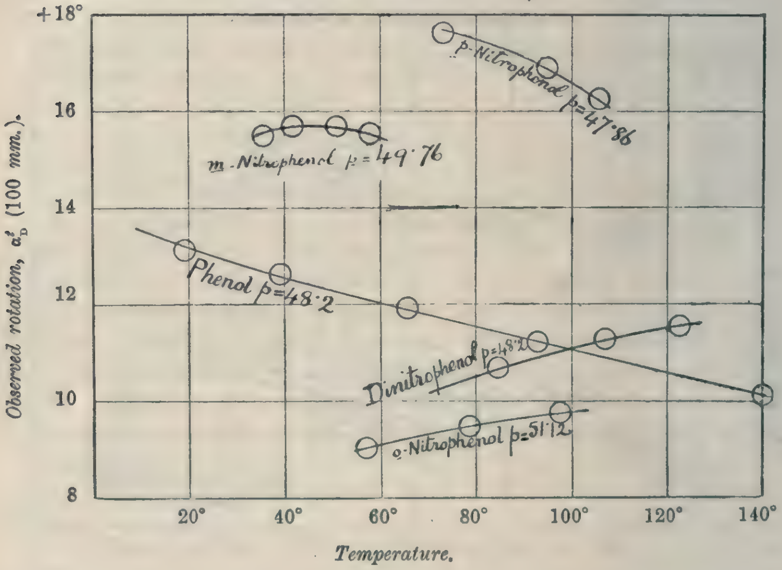
* For 20°, for example, this critical value for specific rotation lies about +18° to +20°.

this point. The rate at which the rotation increases with rise of temperature in pyrogallol ($p = 74{\cdot}93$) is greater than that in catechol solution of about the same concentration, in agreement with the fact that the rotation in the former solution is less than in the latter. In phenol, with its greater solvent influence, the rate of increase of rotation is less than in catechol. In resorcinol there is at first an increase of rotation and then a diminution, a maximum rotation occurring at a temperature of about 60°. This maximum rotation is therefore the critical value at 60°. Our data for phloroglucinol are rather scanty, but it is practically certain that this solvent would show a similar behaviour, and therefore that a maximum rotation probably occurs at a lower temperature than 60°. In quinol only a fall of rotation was observed, but there is doubtless a maximum rotation somewhere about the temperature 40°, which would have a greater value than the maximum in phloroglucinol or in resorcinol. The critical value of the rotation is higher the lower the temperature at which it occurs.

FIG. 3.

Temperature-rotation curves for ethyl tartrate in various solvents.



The above remarks apply equally to the behaviour of α- and β-naphthol and the nitrophenols. In phenol itself it may be noted that whilst the temperature-rotation curves for solutions of high concentration are concave to the point of origin of the diagram, that for a $p=50$ solution is almost a straight line but with a slight convexity, which, as the solutions are diluted, becomes gradually more pronounced. This resembles the behaviour of quinoline (Trans., 1909, **95**, 323), and it is, of course, possible that others of the solvents we have dealt with would show the same behaviour in solutions more dilute than those we have investigated.

The experiments recorded in this paper seem, we think, to justify the conclusion that the chemical constitution of a solvent is not merely reflected—which, of course, it must be—but is reflected in a comparatively simple manner, in the influence of that solvent on the rotation of dissolved ethyl tartrate, and that, conversely, this method might be used for the investigation of chemical constitution. The method differs from that of refractive index and of magnetic rotation, inasmuch as it does not seem possible to calculate any constant increment or decrement for a given group of atoms, for a single atom or for a difference in the linking of an atom in the molecule, but these are certainly indicated qualitatively. There is perhaps a closer connexion between the phenomena we have described and those of absorption spectroscopy. So far as we are able to judge, knowing only one of these methods intimately, the solvent-influence of a compound on the rotation of ethyl tartrate affords a more delicate criterion of chemical constitution than either of the others, as witness, for example, the effect of ortho-, meta-, and para-isomerism, the difference between phenol and anisole, and especially the difference between the *syn*- and *anti*-oximes. We hope to describe the further study of the subject in future papers.

EXPERIMENTAL.

Ethyl Tartrate in Various Solvents.

o-*Chloronitrobenzene.*

$p=25{\cdot}73$:

t …………………	24·7°	30·55°	40·55°	49·2°	58°	82·9°
α_D^t (100 mm.) …	7·7	7·654	7·638	7·61	7·5	7·33

m-*Chloronitrobenzene.*

$p=28{\cdot}43$:

t …………………	36·9°	52·2°	77·4°	89·7°	105·2°
α_D (100 mm.) …	5·754	5·9	6·125	6·046	6·236

p-*Chloronitrobenzene.*

$p=24{\cdot}26$:

t …………………	82·1°	105·2°	117°	128·2°	147·1°
α^t (100 mm.) …	3·735	3·885	4·098	4·106	4·12

Ethyl Tartrate in Various Solvents (continued).

Phenol.

I. $p=14{\cdot}79$:

t	20°	30·75°	52·3°	69·5°	92·4°
α_D^t (100 mm.) ...	—	+5·695	+4·885	+4·525	4·085
$[\alpha]_D^t$	+38·5	+35·47	+30·96	+29·10	26·85

II. $p=23{\cdot}85$:

t	18·8°	20°	32·4°	41·9°	53·5°	65·5	96·9°	130·4°
α_D^t (100 mm.)...	+9·039	—	8·445	8·031	7·586	7·23	6·345	5·666
$[\alpha]_D^t$	34·25	+34·2	32·32	30·98	29·55	28·42	25·7	23·65

III. $p=48{\cdot}2$:

t	19°	20°	39°	65·2°	92·3°	140·6°
α_D^t (100 mm.)...	+13·124	—	12·64	11·95	11·27	10·15
$[\alpha]_D^t$	23·99	23·94	23·44	22·62	21·83	20·54

IV. $p=64{\cdot}78$:

t	20°	20·9°	64·9°	100·3°	126°
α_D^t (100 mm.)......	—	12·853	13·309	13·058	12·7
$[\alpha]_D^t$	17·05	17·10	18·38	18·78	18·52

V. $p=74{\cdot}39$:

t	18·75°	20°	53·5°	76·5°	89·7°
α_D^t (100 mm.)......	11·99	—	13·225	13·62	13·775
$[\alpha]_D^t$	13·78	13·82	15·60	16·38	16·76

VI. $p=79{\cdot}24$:

t	19·95°	20°	55·5°	87·1°	117·2°
α_D^t (100 mm.)......	11·485	11·534	13·248	14·018	14·209
$[\alpha]_D^t$	12·30	12·37	14·62	15·90	16·62

Densities Determined.

I.

t.	*d.*
38·5°	1·0787
45·4	1·0725
66·4	1·0539
78·8	1·0431

II.

t.	*d.*
21·4°	1·1050
37·9	1·0903
58·2	1·0721
78·1	1·0538
99·8	1·0332

III.

t.	*d.*
11·9°	1·1404
33·5	1·1252
46·5	1·1133
74·6	1·0878
99·2	1·0640

IV.

t.	*d.*
14·6°	1·1665
35·5	1·1451
55·8	1·1261
83·4	1·0997

V.

t.	*d.*
16·1°	1·1755
28·7	1·1635
42·0	1·1499
64·7	1·1284

VI.

t.	*d.*
13·5°	1·1837
38·4	1·1606
58·4	1·1412
82·1	1·1176

Ethyl Tartrate in Various Solvents (continued).

Anisole.

I. $p=9·99$:

t	18·2°	20°	27·3°	35·2°
α^{t}_{D} (100 m.)	+ 0·432	—	+ 0·536	+ 0·622
$[\alpha]^{t}_{D}$	+ 4·27	+ 4·5	+ 5·34	+ 6·25

II. $p=24·62$:

t	14·6°	20°	33·2°	46·8°	52·9°	68·9°	72·8°
α^{t}_{D} (100 mm.)	+ 1·602	—	2·068	2·428	2·512	2·952	3·012
$^{t}_{D}$	+ 6·24	6·8	8·20	9·75	10·15	12·11	12·41

III. $p=49·85$:

t	19°	20°	30·6°
α^{t}_{D} (100 mm.)	4·324	—	4·904
$[\alpha]^{t}_{D}$	7·96	8·1	9·12

Densities Determined.

I.		II.		III.	
t.	*d.*	*t.*	*d.*	*t.*	*d.*
17·5°	1·0142	14·9°	1·0424	15·8°	1·0933
25·4	1·0064	32·5	1·0261	25·6	1·0835
—	—	45·5	1·0130	—	—
—	—	55·5	1·0033	—	—

Phenetole.

I. $p=9·99$:

t	19·5°	20°	22·1°	27·1	36·5°
α^{t}_{D} (100 mm.)	+ 0·76	—	0·786	0·822	0·928
$[\alpha]^{t}_{D}$	+ 7·72	7·75	8·00	8·41	9·58

II. $p=24·96$:

t	19·2°	20°	31·6	43·5	50·5
α^{t}_{D} (100 mm.)	+ 1·832	—	2·202	2·51	2·686
$[\alpha]^{t}_{D}$	+ 7·23	7·32	8·79	10·14	10·92

III. $p=51·73$:

t	18·2°	20°	31·0°
α^{t}_{D} (100 mm.)	+ 3·742	—	4·432
$[\alpha]^{t}_{D}$	+ 6·72	+ 6·86	8·05

Densities Determined.

I.		II.		III.	
t.	*d.*	*t.*	*d.*	*t.*	*d.*
18·6°	0·9862	17·9°	1·0161	17·7°	1·0772
25·8	0·9794	28·1	1·0071	26·5	1·0683
—	—	38·3	0·9969	—	—
—	—	48·4	0·9869	—	—

Ethyl Tartrate in Various Solvents (continued).

Diphenyl Ether.

$p=24{\cdot}58$:

t.	18·7°	20°	51·8°	66·0°	76·3°
α_D^t (100 mm.)	+ 1·824	1·95	2·68	2·92	3·288

o-*Nitrophenol.*

I. $p=23{\cdot}89$:

t.	60·1°	81·4°	112·2°
α_D^t (100 mm.)	+ 4·82	4·972	5·007
$[\alpha]_D^t$	+16·20	16·98	17·66

II. $p=51{\cdot}12$:

t.	56·8°	78·2°	97·3°
α_D^t (100 mm.)	+ 9·015	9·486	9·766
$[\alpha]_D^t$	+14·31	15·35	16·08

III. $p=74{\cdot}95$:

t	16°	43·4°	87·3°	115·1°
α_D^t (100 mm.)	+9·142	11·119	12·66	13·056
$[\alpha]_D^t$....................	+9·74	12·14	14·38	14·21

Densities Determined.

I.		II.*		III.	
t.	d.	t.	d.	t.	d.
47·7°	1·2603	56·8°	1·2323	12·5°	1·2558
65·9	1·2416	78·2	1·2086	27·1	1·2385
78·1	1·2295	97·3	1·1878	49·4	1·2164
—	—	—	—	72·5	1·1910

* By interpolation from the determinations for the other two solutions.

o-*Nitroanisole.*

I. $p=9{\cdot}79$:

t..................	17·9°	20°	34·5°	43·3°	53·2°	62·8°
α_D^t (100 mm.)...	+ 3·748	—	3·548	3·490	3·354	3·26
$[\alpha]_D^t$	+30·7	30·6	29·5	29·2	28·3	27·7

II. $p=21{\cdot}17$:

t.	17·4°	20°	29·1°	39·3°	50°	55·8°
α_D^t (100 mm.) ...	6·666	—	6·604	6·472	6·442	6·324
$[\alpha]_D^t$	25·35	25·3	25·4	25·1	25·2	24·8

Densities Determined.

I.		II.	
t.	d.	t.	d.
17·7°	1·2471	14·9°	1·2442
33	1·2319	35	1·2237
42·9	1·2219	53·2	1·2053
59·7	1·2050	66·4	1·1919

Ethyl Tartrate in Various Solvents (continued).

o-*Nitrophenetole.*

I. $p = 25·09$:

t.	18·4°	20°	30·6°	53·3°	65·5°
α^t_D (100 mm.) ...	+ 5·698	—	5·812	5·906	5·896
$[\alpha]^t_D$	+19·11	19·2	19·7	20·41	20·6

II. $p = 39·43$:

t.	15·9°	20°	25·1°	29·1°	42°
α^t_D (100 mm.)...	+ 7·252	—	7·544	7·57	7·848
$[\alpha]^t_D$	+15·41	15·75	16·16	16·27	17·06

Densities Determined.

I.		II.	
t.	d.	t.	d.
17·1°	1·1896	14·6°	1·1948
33·4	1·1734	25·9	1·1833
40·4	1·1659	33·3	1·1757
54·3	1·1524	41	1·1680

p-*Nitrophenol.*

$p = 24·98$:

t.	105·9°	120°
α^t_D (100 mm.)	+ 11·262	10·646
K^t_D	+ 45·09	42·62

$p = 47·86$:

t	72·6°	94·5°	105·7°
α^t_D (100 mm.)	+17·624	16·878	16·274
K^t_D	+36·82	35·27	34·0

p-*Nitroanisole.*

$p = 26·08$:

t.	52·0°	55·8°	64·8°	73·6°	77°
α^t_D (100 mm.)	+ 6·082	6·25	6·515	6·075	6·078

$p = 53·84$:

t	20°	35·1°	44·4°	51·3°	57·6°
α^t_D (100 mm.)...	—	+8·876	9·198	9·376	9·54
$[\alpha]^t_D$	+12·5	+13·63	14·23	14·58	14·91

Densities Determined.

t	35·1°	41·4°	48°	57·2°
d	1·2101	1·2038	1·1974	1·1883

p-*Nitrophenetole.*

$p = 24·37$:

t	50·1°	57·3°	67·3°	82·5°
α^t_D (100 mm.) ...	+3·88	3·995	4·21	4·345

$p = 49·66$:

t	49·4°	54·4°	66·6°	69·7°
α^t_D (100 mm.)	+6·475	6·73	7·175	7·28

m-*Nitrophenol.*

$p = 49·76$:

t	35·4°	41·4°	50·3°	57·7°
α^t_D (100 mm.)......	+15·5	15·68	15·665	15 55

Ethyl Tartrate in Various Solvents (continued).

2 : 4-*Dinitrophenol* (m. p. 114·5°).

$p = 75{\cdot}15$:

t	84·5°	107°	121·5°
α^{t} (100 mm.)	+10·696	11·272	11·564

Catechol.

$p = 74{\cdot}81$:

t	41·4°	68·9°	94·3°	103·7°
α^t_D (100 mm.)......	+12·12	13·04	13·40	13·53

Resorcinol.

$p = 74{\cdot}12$:

t	15·9°	47·7°	74·3°	104·2°
α^t_D (100 mm.)......	+16·25	16·86	16·89	16·644

Quinol.

$p = 74{\cdot}47$:

t	70·3°	105°	136·5°
α^t_D (100 mm.)	+18·1	17·5	16·53

Pyrogallol.

$p = 74{\cdot}93$:

t	49·5°	78·9°	108·6°
α^t_D (100 mm.)	11·884	12·868	13·344

Phloroglucinol.

$p = 74{\cdot}33$:

t	69·5°	93·6°	104·1°
α^t_D (100 mm.)	+17·48	17·43	17·10

α-Naphthol.

$p = 25{\cdot}24$:

t	105·6°	121·5°
α^t_D (100 mm.)	+7·276	6·732

β-Naphthol.

$p = 29{\cdot}01$:

t	132·7°	150°
α^t_D (100 mm.)	+10·92	+9·988

p-*Benzoquinone.*

$p = 74{\cdot}98$:

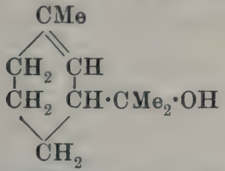
t	87·5°	115°	122·9°
α^t_D (100 mm.)	+10·804	10·968	11·128

THE UNIVERSITY,
GLASGOW.

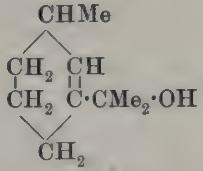
CCXXIII.—*Experiments on the Synthesis of the Terpenes. Part XIV. Synthesis of* d- *and* l-Δ^5-m-*Menthenol*(8), dl-Δ^4-m-*Menthenol*(8) *and their Derivatives.*

By WILLIAM HENRY PERKIN, jun.

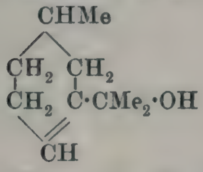
OF the six possible menthenols of the meta-series,* the following four have, so far, been synthesised:



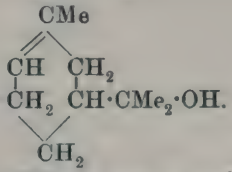
Δ^1-(Dihydrocarvestrenol)
(Trans., 1907, **91**, 498.)



(Δ^2.)
(Trans., 1905, **87**, 1101.)

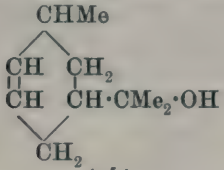


(Δ^3) (Trans., 1905, **87**, 1099; compare this vol., p. 1029.)



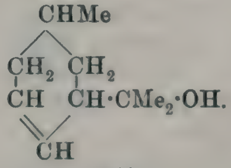
Δ^6-(Dihydro*iso*carvestrenol).
(Trans., 1908, **93**, 1887.)

The present communication contains an account of the synthesis of the remaining two, namely:



(Δ^5.)

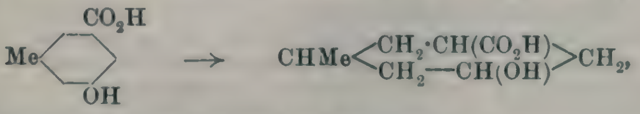
and



(Δ^4.)

Of the former, the *d*- and *l*- and *dl*-modifications have been prepared, whereas of the latter only the *dl*-modification was obtained, and that in very small quantity.

A short time since (Trans., 1909, **95**, 1889), Meldrum and Perkin showed that 5-hydroxy-*m*-toluic acid is reduced by sodium and *iso*amyl alcohol to 1-methyl*cyclo*hexan-5-ol-3-carboxylic acid †:



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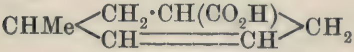
* Menthenols of the type of terpineol are here referred to.

† In the paper referred to, this acid was called "1-methyl*cyclo*hexan-3-ol-5-carboxylic acid," but the alternative numbering is more suitable.

and, in the present communication, it is shown that this reduction may also be effected in alcoholic solution, provided that the alcohol has been completely dehydrated by distillation over calcium.

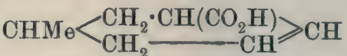
When 1-methyl*cyclo*hexan-5-ol-3-carboxylic acid is treated with hydrobromic acid, it is readily converted into 5-bromo-1-methyl*cyclo*hexane-3-carboxylic acid, and the ester of this acid, when digested with diethylaniline, yields a mixture of the esters of the acids:



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CH(CO_2H)}\\ \mathrm{CH{=\!=\!=\!=}CH}\end{matrix}>\mathrm{CH_2}$$

1-Methyl-Δ^5-*cyclo*hexene-3-carboxylic acid.

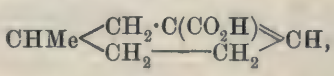
and



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CH(CO_2H)}\\ \mathrm{CH_2{-\!-\!-\!-}CH}\end{matrix}\geqslant\mathrm{CH}$$

1-Methyl-Δ^4-*cyclo*hexene-3-carboxylic acid.

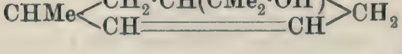
and these acids, of which the former is produced in by far the larger quantity,* were separated by the fractional crystallisation of their calcium salts. The constitution of the former of these acids (Δ^5) was demonstrated by the examination of the products of the oxidation of Δ^5-*m*-menthenol(8) obtained from its ester by the action of magnesium methyl iodide (p. 2132). The constitution of the other acid (Δ^4) was proved by the fact that, when boiled with concentrated aqueous potassium hydroxide, it is converted into 1-methyl-Δ^3-*cyclo*hexene-3-carboxylic acid:



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot C(CO_2H)}\\ \mathrm{CH_2{-\!-\!-}CH_2}\end{matrix}\geqslant\mathrm{CH},$$

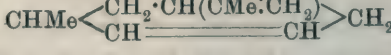
the $\beta\gamma$-unsaturated acid becoming $\alpha\beta$- in the usual manner.

Ethyl *dl*-1-methyl-Δ^5-*cyclo*hexene-3-carboxylate reacts readily with magnesium methyl iodide with the formation of dl-Δ^5-m-*menthenol*(8) (b. p. 115—117°/30 mm.), and this, when boiled with aqueous oxalic acid, yields *dl*-$\Delta^{5:8(9)}$-*m*-menthadiene (b. p. 175—176°):



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CH(CMe_2\cdot OH)}\\ \mathrm{CH{=\!=\!=\!=\!=}CH}\end{matrix}>\mathrm{CH_2}$$

and



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CH(CMe{:}CH_2)}\\ \mathrm{CH{=\!=\!=\!=\!=}CH}\end{matrix}>\mathrm{CH_2}.$$

Under similar conditions, ethyl *dl*-1-methyl-Δ^4-*cyclo*hexenecarboxylate yields Δ^4-*m*-menthenol(8) (b. p. 115—117°/30 mm.) and $\Delta^{4:8(9)}$-*m*-menthadiene (b. p. 175—177°):

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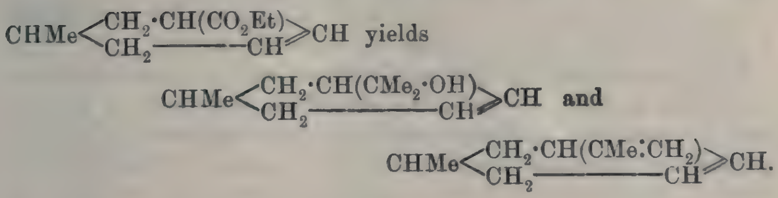
* It has often been observed, in cases where two isomeric unsaturated acids are formed by the elimination of hydrogen bromide from a bromo-acid, that very slight changes in the conditions of experiment often effect in a remarkable manner the proportions of the isomerides produced. Two experiments were made on the elimination of hydrogen bromide from ethyl 5-bromo-1-methyl*cyclo*hexane-3-carboxylate by means of diethylaniline. In the one the yield of 1-methyl-Δ^4-*cyclo*hexene-3-carboxylic acid obtained on hydrolysis was 5 per cent., in the other, apparently under the same conditions, the yield was less than 1 per cent.



$$\mathrm{CHMe}\!<\!\begin{matrix}\mathrm{CH_2\cdot CH(CO_2Et)}\\ \mathrm{CH_2}\text{———}\mathrm{CH}\end{matrix}\!>\!\mathrm{CH} \text{ yields } \mathrm{CHMe}\!<\!\begin{matrix}\mathrm{CH_2\cdot CH(CMe_2\cdot OH)}\\ \mathrm{CH_2}\text{————}\mathrm{CH}\end{matrix}\!>\!\mathrm{CH} \text{ and } \mathrm{CHMe}\!<\!\begin{matrix}\mathrm{CH_2\cdot CH(CMe{:}CH_2)}\\ \mathrm{CH_2}\text{————}\mathrm{CH}\end{matrix}\!>\!\mathrm{CH}.$$

Resolution of dl-1-*Methyl*-Δ^5-cyclo*hexene*-3-*carboxylic Acid and Preparation of the* d- *and* l-*Modifications of* Δ^5-m-*Menthenol*(8).

As the amount of pure *dl*-1-methyl-Δ^5-*cyclo*hexene-3-carboxylic acid which had accumulated during these experiments amounted to more than 160 grams, it was thought that it would be interesting to attempt its resolution, and then to convert the active acids into the corresponding menthenols and menthadienes. This was ultimately accomplished with the aid of either *l*-menthylamine or quinine, the salt produced in both cases being the salt of the dextro-acid.

The *l*-menthylamine salt, after repeated recrystallisation, had $[\alpha]_D -1{\cdot}7°$, and from this salt the acid was regenerated and converted into its ester and the corresponding menthenol and terpene by processes already described in the case of the *dl*-acid. The observed rotations of these substances may be conveniently tabulated thus:

	$[\alpha]_D$.
d-1-Methyl-Δ^5-*cyclo*hexene-3-carboxylic acid	$+33{\cdot}1°$
Ethyl *d*-1-methyl*cyclo*hexenecarboxylate	$+30{\cdot}5$
d-Δ^5-*m*-Menthenol(8)	$+36{\cdot}7$
d-$\Delta^{5\,8(9)}$-*m*-Menthadiene	$+29{\cdot}6$

After the *d*-acid had been removed, as far as practicable, by treatment with *l*-menthylamine and quinine, the *l*-1-methyl-Δ^5-*cyclo*hexene-3-carboxylic acid, contained in the mother liquor of these salts, was nearly pure, since its rotation was $[\alpha]_D -30{\cdot}9°$, as compared with the rotation $[\alpha]_D +33{\cdot}1°$ of the corresponding *d*-acid.

From this *l*-acid the same derivatives were prepared as in the case of the *d*-acid, and these and their rotations may again be tabulated:

	$[\alpha]_D$.
l-1-Methyl-Δ^5-*cyclo*hexene-3-carboxylic acid	$-30{\cdot}9°$
Ethyl *l*-1-methyl*cyclo*hexenecarboxylate	$-27{\cdot}4$
l-Δ^5-*m*-Menthenol(8)	$-32{\cdot}6$
l-$\Delta^{5:8(9)}$-*m*-Menthadiene	$-25{\cdot}3$

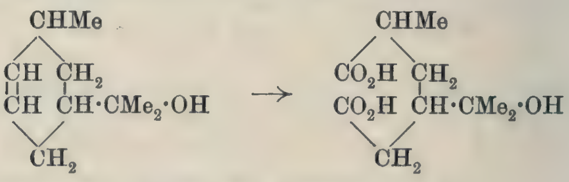
The constitutions assigned to these active menthenols and menthadienes, and indirectly therefore those of the corresponding inactive substances and also that of 1-methyl-Δ^5-*cyclo*hexene-3-carboxylic acid, were proved in the following manner.

Pure *d*-Δ^5-*m*-menthenol(8) was oxidised with permanganate and then with dichromate under the conditions described on p. 2143, and the resulting acid converted into the ethyl ester, which was purified by fractional distillation under diminished pressure. The ester, $C_{12}H_{20}O_4$, thus obtained distilled at 188—190°/20 mm., and had $[\alpha]_D$ $-18{\cdot}7°$.

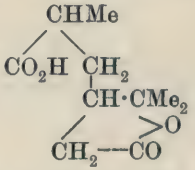
When this ester was hydrolysed, it yielded a mixture of two isomeric lactonic acids, $C_{10}H_{16}O_4$, which melt at 102° and 136° respectively, and are obviously the *cis*- and *trans*-lactones of α-methyl-γ-hydroxy*iso*propyladipic acid:

$$CO_2H{\cdot}CHMe{\cdot}CH_2{\cdot}CH(CMe_2{\cdot}OH){\cdot}CH_2{\cdot}CO_2H.$$

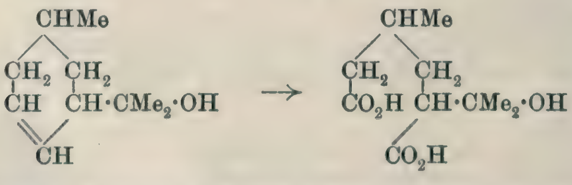
The formation of this acid by the oxidation of Δ^5-*m*-menthenol(8) may be expressed in the following manner:



and its easy conversion into the lactone:



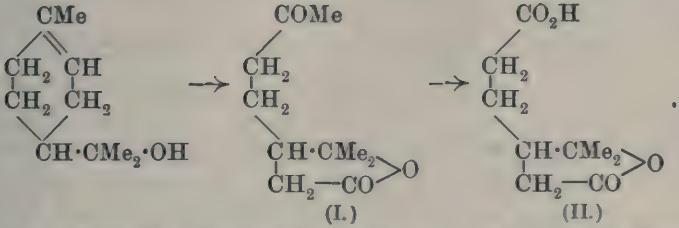
proves that the menthenol from which it is derived must have the double linking in the Δ^5-position, since the dibasic acid which might result from the oxidation of the menthenol of the other alternative constitution (Δ^4):



would hardly be expected to pass into a lactone.

The oxidation of *d*-Δ^5-*m*-menthenol(8) is very similar to that of ordinary terpineol, which, with chromic acid, yields methoethylheptanonolide (I), and then, with hypobromite, homoterpenylic acid

(II) (Wallach, *Ber.*, 1895, **28**, 1773; Tiemann and Semmler, *ibid.*, 2141):

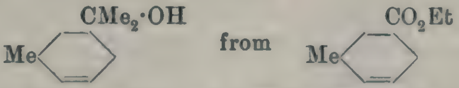


(I.) (II.)

A similar series of oxidations carried out with *l*-Δ^5-*m*-menthenol(8) gave again the ester, $C_{12}H_{20}O_4$, of the mixed lactonic acids. This had $[\alpha]_D$ +17·4°, and yielded, on hydrolysis, the *cis*- and *trans*-lactones of melting points 102° and 136°, which had been obtained from the *d*-modification. Moreover, it is curious that, whilst the ester, $C_{12}H_{20}O_4$, was, in both cases, optically active, the lactones obtained on hydrolysis, although they still contain two asymmetric carbon atoms, should prove to be inactive.

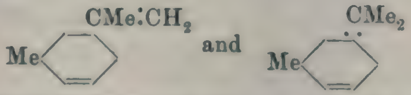
These oxidation experiments show conclusively not only that the two active series tabulated on p. 2131 represent *d*- and *l*-modifications of the same substances, but also that these substances have the constitutions which have been assigned to them.

In connexion with this series of researches on the synthesis of the terpenes, there is one point of importance which should be made quite clear. When a menthenol is synthesised from the ester of the corresponding acid by the action of magnesium methyl iodide, for example:

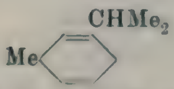


the menthenol which is obtained is quite pure and homogeneous.

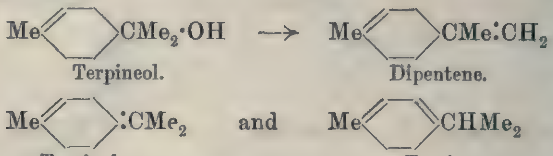
When, however, water is eliminated from such a menthenol, the resulting menthadiene is probably, as a rule, not a homogeneous substance, but may consist of a mixture, in varying proportions, of the isomerides:



and possibly, owing to intramolecular change, the third isomeride of the type:



may also be present. It is well known, especially from the researches of Wallach, that ordinary terpineol, on treatment with dehydrating agents, yields not only dipentene, but also terpinolene and α-terpinene:

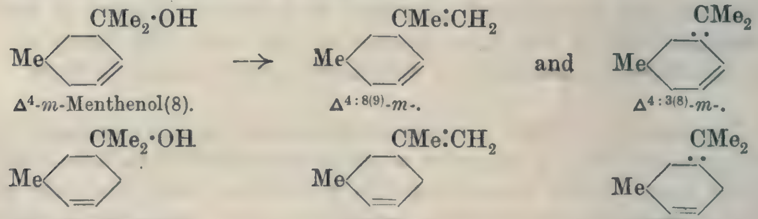


Terpineol. Dipentene.

Terpinolene. α-Terpinene.

The conversion of terpineol into terpinolene appears to take place most readily when dilute acids are used as the dehydrating agent. Thus, Baeyer (*Ber.*, 1894, **27**, 447) recommends 30 per cent. oxalic acid as the best reagent for converting terpineol into terpinolene.

In the present communication it is stated that the reagent which was found most suitable for the elimination of water from Δ^4- and Δ^5-*m*-menthenol(8) was 6 per cent. oxalic acid, and it seems therefore very probable that the products obtained in each case may be mixtures of at least two menthadienes:



Δ^4-*m*-Menthenol(8). $\Delta^{4:8(9)}$-*m*-. $\Delta^{4:3(8)}$-*m*-.

Δ^5-*m*-Menthenol(8). $\Delta^{5:8(9)}$-*m*-. $\Delta^{5:3(8)}$-*m*-.

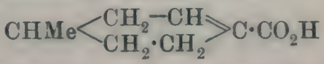
It would be difficult to separate and identify such isomeric products of the elimination of water even if large quantities of the menthenols were available, and, in the present case, where the preparation of even small quantities of material is very laborious, this problem cannot, in the meantime, be solved. It has therefore been decided to retain for the present the names $\Delta^{4:8(9)}$- and $\Delta^{5:8(9)}$-*m*-menthadiene for the hydrocarbons, and the determination of the exact nature of these products of dehydration must be left until a better method for their preparation has been discovered. When larger quantities of material are available, an effort will also be made accurately to determine the physical constants of all the substances mentioned in this paper.

The probability that substances of the terpinolene type are frequently produced during the elimination of water from the menthenols according to the process:

$$>CH \cdot CMe_2 \cdot OH \longrightarrow >C\colon CMe_2$$

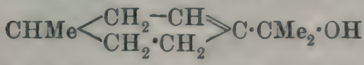
suggests an explanation for some of the remarkable results which have been obtained, more particularly during the course of the investigation of optically active menthenols and menthadienes. In the first place, it is important to note that the above process cannot take place when the $>CMe_2\cdot OH$ group is attached to a doubly linked carbon atom, as in $\gg C\cdot CMe_2\cdot OH$. Apart from fundamental intramolecular change, which both chemical properties and physical measurements show to be most improbable, menthenols containing this grouping can only yield conjugated menthadienes containing the grouping $\gg C\cdot CMe{:}CH_2$, and there can be little doubt that the several synthetical menthadienes of this type which have already been described (compare this vol., p. 2154) are pure individuals.

Some time since, Kay and Perkin (Trans., 1906, **89**, 840) resolved *dl*-1-methyl-Δ^3-*cyclo*hexene-4-carboxylic acid:



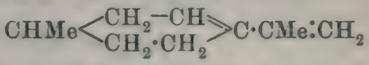
$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\gg\mathrm{C{\cdot}CO_2H}$$

into its active constituents, and prepared from the *d*- and *l*-acids, *d*- and *l*-*p*-menthenol(8) and *d*- and *l*-$\Delta^{3:8(9)}$-*p*-menthadiene:



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\gg\mathrm{C{\cdot}CMe_2{\cdot}OH}$$

and

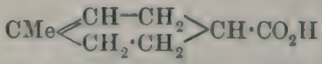


$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\gg\mathrm{C{\cdot}CMe{:}CH_2}$$

in the usual manner. Taking the *d*-series as the example, the optical activity of these substances may be conveniently tabulated:

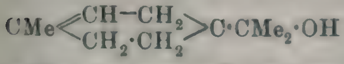
	$[\alpha]_D$.
d-1-Methyl-Δ^3-*cyclo*hexene-4-carboxylic acid	+101·1°
Ethyl *d*-1-methyl*cyclo*hexenecarboxylate	+86·5
d-Δ^3-*p*-Menthenol(8)	+67·0
d-$\Delta^{3:8(9)}$-*p*-Methadiene	+98·2

It will be observed that, in this case, the menthadiene has a much higher rotation than the menthenol from which it is produced by the elimination of water. Subsequently Fisher and Perkin (Trans., 1908, **93**, 1872) resolved *dl*-1-methyl-Δ^1-*cyclo*hexene-4-carboxylic acid:



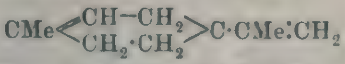
$$\mathrm{CMe}\ll\begin{matrix}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}>\mathrm{CH{\cdot}CO_2H}$$

and prepared from the active acids, the menthenols (terpineols) and menthadienes (limonenes):



$$\mathrm{CMe}\ll\begin{matrix}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}>\mathrm{C{\cdot}CMe_2{\cdot}OH}$$

and

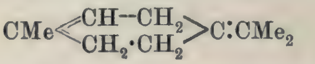


$$\mathrm{CMe}\ll\begin{matrix}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}>\mathrm{C{\cdot}CMe{:}CH_2}$$

in the same way. Taking, as the example, the *l*-series, the following values were observed as the rotations of these substances:

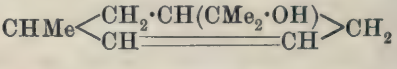
	$[\alpha]_D$.
l-1-Methyl-Δ^1-*cyclo*hexene-4-carboxylic acid	−58°
Ethyl *l*-methyl*cyclo*hexenecarboxylate	−52
l-Δ^1-*p*-Menthenol(8)	−46·6
l-$\Delta^{1:8(9)}$-*p*-Menthadiene	−5·0

It is clear that the relationship between the values for the different substances given in this table are very similar to those shown in the preceding table, with the exception of the striking differences in the rotations of the menthadienes. It is well known that the active limonenes are somewhat easily racemised with formation of dipentene, and for this reason we were careful to conduct the elimination of water at the ordinary temperature with the aid of magnesium methyl iodide, and we were surprised to find that, instead of obtaining a hydrocarbon of higher rotation than the menthenol (terpineol) (*l*-limonene has $[\alpha]_D -120°$), the rotation had decreased to $-5°$. No doubt this result was partly due to racemisation, because we were able to show that the substance contained considerable quantities of dipentene.* But it is very probable that the low rotation is also due to the hydrocarbon containing considerable quantities of terpinolene:



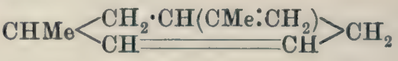
$$\mathrm{CMe}<\begin{matrix}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}>\mathrm{C{:}CMe_2}$$

which is of necessity inactive. In the present communication it is shown that, when *d*-Δ^5-*m*-menthenol(8) ($[\alpha]_D +36{\cdot}7°$):



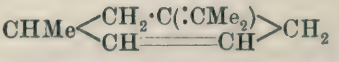
$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2{\cdot}CH(CMe_2{\cdot}OH)}\\ \mathrm{CH{=\!=\!=}CH}\end{matrix}>\mathrm{CH_2}$$

is digested with 6 per cent. oxalic acid, the resulting *d*-$\Delta^{5:8(9)}$-*m*-menthadiene ($[\alpha]_D +29{\cdot}6°$):



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2{\cdot}CH(CMe{:}CH_2)}\\ \mathrm{CH{=\!=\!=}CH}\end{matrix}>\mathrm{CH_2}$$

has a lower rotation than the menthenol instead of a higher one, as might have been expected from the experiments of Kay and Perkin just referred to. This would seem to indicate that this terpene may contain $\Delta^{5:3(8)}$-*m*-menthadiene:



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2{\cdot}C({:}CMe_2)}\\ \mathrm{CH{=\!=\!=}CH}\end{matrix}>\mathrm{CH_2}$$

and the rather high numbers obtained for the refractive power as the result of preliminary physical measurements seem to support this view. If this is the case, one of the asymmetrical carbon atoms of the menthenol will have disappeared during the formation of this substance by the elimination of water, and this may be the explanation of the drop in the rotation.

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* As the presence of dipentene was only proved qualitatively, the statement (*loc. cit.*, p. 1873) that the hydrocarbon of $[\alpha]_D -5°$ consisted essentially of dipentene should not have been made, and is probably incorrect.

EXPERIMENTAL.

Preparation of 1-*Methyl*-Δ^5-cyclo*hexene-3-carboxylic Acid and* 1-*Methyl*-Δ^4-cyclo*hexene-3-carboxylic Acid.*

In the first experiments (*Trans.*, 1909, **95**, 1897), the reduction of 5-hydroxy-*m*-toluic acid was carried out in *iso*amyl-alcoholic solution with sodium, but it was subsequently found that the acid is also reduced, although with some difficulty, when its solution in absolute alcohol * is treated with sodium. The pure acid, in quantities of 50 grams, dissolved in alcohol (1250 grams) was reduced by the rapid addition of sodium (180 grams) substantially in the manner described in detail in the case of the reduction of 4-hydroxy-*o*-toluic acid (Trans., 1909, **95**, 1876). After extracting in the usual way, the acid was reduced a second time under the same conditions, and in all about 1 kilogram of the hydroxy-acid was worked up, and yielded about 840 grams of reduction product. This acid (which consists for the most part of *trans*-1-methyl*cyclo*hexan-5-ol-3-carboxylic acid, compare *loc. cit.*, p. 1891), in quantities of 50 grams, was mixed with three volumes of fuming hydrobromic acid (saturated at 0°), and, after remaining for two days at the ordinary temperature, the liquid was heated on the water-bath for two hours, when it separated into two layers. The product was mixed with water, extracted twice with ether, and, after drying and evaporating, the crude bromo-acid was digested with alcohol (200 c.c.) and sulphuric acid (20 c.c.) for four hours on the water-bath, and then left for twenty-four hours. On adding water, the heavy bromo-ester was precipitated, and was extracted with ether, the ethereal solution was thoroughly washed with water and dilute sodium carbonate, carefully dried, evaporated, and the crude ester heated to boiling with three volumes of diethylaniline for eight hours. Excess of dilute hydrochloric acid was then added, the unsaturated ester extracted with ether, the ethereal solution washed first with dilute hydrochloric acid, and then with sodium carbonate, and distilled in steam.†

The volatile ester was extracted with ether, dried, and distilled, when almost the whole quantity passed over at 140—150°/100 mm., and weighed 710 grams. In order to avoid any possibility of intramolecular change (compare p. 2146), the hydrolysis of this ester was very carefully carried out. The ester was gradually mixed with exactly the quantity of alcoholic potassium hydroxide required for hydrolysis, the addition extending over about a week, and after remaining for ten days in all, at the ordinary temperature, water was added, and any non-hydrolysed ester extracted with ether. The aqueous solution was nearly neutralised with hydrochloric acid, saturated with carbon dioxide, evaporated until quite free from alcohol, acidified, and the unsaturated acids were extracted with ether and distilled, when almost the whole quantity passed over at 140—142°/20 mm. It has already been mentioned (p. 2130) that this acid is a mixture of 1-methyl-Δ^5-*cyclo*hexene-3-carboxylic acid and 1-methyl-Δ^4-*cyclo*hexene-3-carboxylic acid, and, in order to separate these, the oil was digested with much water and excess of freshly precipitated calcium carbonate on the water-bath for several hours. After filtering and concentrating considerably, the calcium salt of the Δ^5-acid separated as a voluminous mass of balls of needles, and the mother liquor, on concentration, deposited further crops of this same salt.

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* Distilled over calcium, see footnote, Trans., 1909, **95**, 1876.

† When all the unsaturated ester had passed over, a considerable amount of a viscid, brown residue remained in the distilling flask. This was extracted with ether, and yielded on treatment with hydrogen bromide, diethylaniline, etc., exactly as described above, a further quantity of unsaturated ester, which was added to that obtained as the result of the first operation.

After a certain concentration had been reached, the brown mother liquors yielded a crop of calcium salt quite different in appearance from the calcium salt of the Δ^5-acid. This salt was decomposed by hydrochloric acid, and the acid extracted, distilled under diminished pressure, and again made into calcium salt, and by repeating the process of fractional crystallisation, the two calcium salts were, as far as could be seen, completely separated.

dl-1-*Methyl*-Δ^5-cyclo*hexene*-3-*carboxylic Acid.*

In preparing this acid, the pure calcium salt, obtained in the way described in the last section, was decomposed by dilute hydrochloric acid, the oily acid extracted with ether, the ethereal solution washed, dried, and evaporated, and the acid distilled under diminished pressure:

0·1957 gave 0·4897 CO_2 and 0·1561 H_2O. C = 68·2; H = 8·8.

$C_8H_{12}O_2$ requires C = 68·5; H = 8·6 per cent.

dl-1-*Methyl*-Δ^5-cyclo*hexene*-3-*carboxylic acid* is a rather viscid oil, which distils at 145°/20 mm. or 177—180°/100 mm., and, especially when warm, has a very unpleasant odour. The highly characteristic *calcium* salt appears to have the formula $(C_8H_{11}O_2)_2Ca,5H_2O$:

0·1908 of the air-dried salt lost 0·0411 at 100°, and yielded 0·0627 $CaSO_4$. $H_2O = 21·54$; Ca = 9·67.

0·1332 lost 0·0287 at 100°. $H_2O = 21·54$.

0·1128 gave 0·0370 $CaSO_4$. Ca = 9·65.

$(C_8H_{11}O_2)_2Ca,5H_2O$ requires $H_2O = 22·06$; Ca = 9·8 per cent.

These analyses, for which I am indebted to Dr. A. N. Meldrum, were carried out with three different preparations of the salt.

Ethyl dl-1-*Methyl*-Δ⁵-cyclo*hexene*-3-*carboxylate*.—This ester was prepared by warming the acid (15 grams) with alcohol (100 c.c.) and sulphuric acid (6 c.c.) for three hours on the water-bath. Water was then added, the ester extracted with ether, the ethereal solution washed with water and sodium carbonate, dried, evaporated, and the oil distilled under diminished pressure:

0·1117 gave 0·2914 CO_2 and 0·0984 H_2O. C=71·2; H=9·8.

$C_{10}H_{16}O_2$ requires C=71·4; H=9·5 per cent.

This ester distils at 141—143°/100 mm., and possesses a penetrating and most unpleasant odour.

dl-Δ^5-m-*Menthenol*(8) *and* dl-$\Delta^{5:8(9)}$-m-*Menthadiene*.

In preparing *dl*-Δ^5-*m*-menthenol(8), ethyl *dl*-1-methyl-Δ^5-*cyclo*hexene-3-carboxylate (10 grams) was added to an ethereal solution of magnesium methyl iodide containing 4 grams of magnesium, all rise of temperature above 25° being checked by cooling with water. After twenty-four hours, the product was decomposed by the addition of water and then dilute hydrochloric acid, the ethereal solution washed well, dried, and evaporated, and the residue mixed with a solution of 2 grams of potassium hydroxide in methyl alcohol, and left for two days in order that any trace of unchanged ester might be removed. The neutral oil was then precipitated by water, extracted, and distilled under diminished pressure:

0·1515 gave 0·4319 CO_2 and 0·1604 H_2O. C=77·7; H=11·8.

$C_{10}H_{18}O$ requires C=77·9; H=11·7 per cent.

dl-Δ^5-m-*Menthenol*(8) distils at 115—117°/30 mm., and is a viscid, colourless oil, possessing a strong and pleasant odour of terpineol and peppermint. In order to convert this tertiary alcohol into the corresponding hydrocarbon, it was boiled with 6 per cent. aqueous oxalic acid in a reflux apparatus for three hours, then distilled in steam, and the distillate extracted with ether. After carefully drying over potassium carbonate and removing the ether by evaporation, the residual oil distilled almost completely at 172—180°, and two distillations over sodium yielded the pure terpene:

0·1192 gave 0·3834 CO_2 and 0·1282 H_2O. C=87·9; H=11·9.

$C_{10}H_{16}$ requires C=88·2; H=11·8 per cent.

dl-$\Delta^{5:8(9)}$-m-*Menthadiene* distils at 175—176°/765 mm., and has a pronounced odour of lemons, which, however, is quite distinct from that of limonene.

Resolution of dl-1-*Methyl*-Δ^5-cyclo*hexene-3-carboxylic Acid.*

The resolution of this acid into its active modifications may be accomplished with the aid either of *l*-menthylamine or of quinine.

I. *Experiments with* l-*Menthylamine.*—The acid available for this purpose weighed rather more than 160 grams, and was divided into two parts. The oil (80 grams) was dissolved in 570 c.c. of *N*/10-sodium carbonate, heated to boiling, and mixed with a solution of pure *l*-menthylamine hydrochloride (120 grams), when a viscid syrup separated which soon began to crystallise. After remaining overnight, the aqueous liquid was decanted * from the semi-solid cake; the latter was then washed, and left in contact with porous porcelain until quite hard and dry; it then weighed 105 grams. The crude salt was rubbed with a little pure acetone in a mortar, quickly filtered, and the colourless residue crystallised from acetone, from which it separated in long, slender needles:

0·9028, made up to 20 c.c. with alcohol, gave α_D −0·48° in a 2-dcm. tube at 16°, whence $[\alpha]_D$ −5·3°.

After two more crystallisations, the salt had $[\alpha]_D$ −2·8°, and after two further crystallisations, $[\alpha]_D$ −1·7°, and it therefore consists of the *l*-menthylamine salt of *d*-1-methyl-Δ^5-*cyclo*hexene-3-carboxylic acid:

0·1108 gave 5·1 c.c. N_2 at 18° and 760 mm. N = 5·3.

$C_{18}H_{33}O_2N$ requires N = 4·7 per cent.

By extracting the porous plates which had been employed in purifying the crude *l*-menthylamine salt as explained above, and carefully working up all mother liquors, about 120 grams of the pure *l*-menthylamine salt of rotation $[\alpha]_D$ −1·7° were ultimately obtained, and this was decomposed by dilute sodium hydroxide, and after the *l*-menthylamine had been extracted with ether, the alkaline solution was acidified, the active acid extracted with ether, and distilled under diminished pressure:

0·1931 gave 0·4819 CO_2 and 0·1532 H_2O. C = 68·1; H = 8·8.

$C_8H_{12}O_2$ requires C = 68·5; H = 8·6 per cent.

d-1-*Methyl*-Δ^5-cyclo*hexene-3-carboxylic acid* boils at 145°/20 mm., and has the following rotation:

1·0088, made up to 20 c.c. with ethyl acetate, gave α_D +3·34° in a 2-dcm. tube at 16°, whence $[\alpha]_D$ +33·1°.

Ethyl d-1-*Methyl*-Δ^5-cyclo*hexene-3-carboxylate* was prepared by mixing the acid (40 grams) with alcohol (200 grams) and sulphuric acid (15 c.c.), and, after remaining at the ordinary temperature for a week, water was added, and the oily ester extracted with ether. The ethereal solution was well washed with sodium carbonate, dried, and evaporated. The ester distilled at 140—141°/100 mm. as a mobile liquid with a penetrating and very unpleasant odour:

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* These aqueous liquors yield, on acidifying and extracting with ether, nearly 10 grams of acid, which was used in another experiment.

0·1856 gave 0·4849 CO_2 and 0·1626 H_2O. C=71·2; H=9·8.

$C_{10}H_{16}O_2$ requires C=71·4; H=9·5 per cent.

0·9520, made up to 20 c.c. with ethyl acetate, gave α_D +2·91° in a 2-dcm. tube at 16·5°, whence $[\alpha]_D$ +30·5°.

II. *Experiment with Quinine.*—This method of resolution, which appears to give good results, was carried out subsequent to the experiments with *l*-menthylamine, just described, and with a comparatively small quantity of the *dl*-acid. The acid (45 grams) was digested in ethyl acetate solution with quinine (125 grams), and the clear solution left in the ice-chest for eight days, when a considerable quantity of a crystalline crust had separated. This was collected, twice recrystallised from ethyl acetate, and then decomposed in the usual manner, when it yielded an acid which distilled at 142°/20 mm., which had the following high rotation:

1·0052, made up to 20 c.c. with ethyl acetate, gave α_D +3·31° in a 2-dcm. tube at 16°, whence $[\alpha]_D$ +32·9°.

It would have been interesting again to have converted the active acid into the quinine salt in order to determine whether a higher rotation would have resulted than the +33·1° obtained in the case of the resolution with *l*-menthylamine, but unfortunately the acid was accidentally lost.

d-Δ^5-m-*Menthenol*(8) *and* d-$\Delta^{5:8(9)}$-m-*Menthadiene.*

The conversion of ethyl *d*-1-methyl-Δ^5-*cyclo*hexene-3-carboxylate into *d*-Δ^5-*m*-menthenol(8) was brought about by adding the ester (15 grams) to an ethereal magnesium methyl iodide solution containing 6 grams of magnesium, the temperature being kept below 25° during mixing and subsequently. After twenty-four hours, the product was decomposed by water and hydrochloric acid in the usual manner, the ethereal solution washed well, dried, and evaporated. The residual oil distilled remarkably constantly at 115°/30 mm.:

0·1438 gave 0·4120 CO_2 and 0·1551 H_2O. C=78·1; H=12·0.

$C_{10}H_{18}O$ requires C=77·9; H=11·7 per cent.

0·8810, made up to 20 c.c. with alcohol, gave α_D +3·25° in a 2-dcm. tube at 16°, whence $[\alpha]_D$ +36·7°.

d-Δ^5-m-*Menthenol*(8) is a colourless, rather viscid oil, possessing a strong odour of terpineol and menthol; even when kept for several months, it showed no signs of crystallising, and an attempt to prepare a crystalline phenylurethane was also unsuccessful.

When a drop of sulphuric acid is added to the solution of this menthenol in acetic anhydride, a faint pink colour, like dilute permanganate, is produced, and, on keeping, this gradually becomes more violet and then fades. The menthenol (5 c.c.) was shaken with dilute sulphuric acid (350 c.c. of 5 per cent.) for seven days on the machine, the product distilled in a current of steam, and the volatile oil extracted and distilled under the ordinary pressure, when almost the whole quantity passed over at about 203°, and evidently consisted of the unchanged menthenol, only traces at most of the corresponding terpene having been produced. The solution in the steam distillation flask yielded, after saturation with ammonium sulphate and extraction with ether, about 0·5 gram of a syrup, which gradually crystallised and evidently consisted of the corresponding terpin, but the quantity was too small for purification. When the menthenol was mixed with three volumes of fuming hydrobromic acid (saturated at 0°), it did not appear to dissolve, and, even after several weeks, no solid additive product had been formed.

d-$\Delta^{5:8(9)}$-m-*Menthadiene.*—This terpene is formed when *d*-Δ^5-*m*-menthenol(8) (10 grams) is digested with aqueous oxalic acid (100 c.c. of 6 per cent.) in a reflux apparatus for six hours, and the product distilled in a current of steam.

The volatile oil was extracted with ether, the ethereal solution dried very carefully, evaporated, and the residue distilled, when almost the whole passed over below 180°, and, after twice fractionating over sodium, the terpene distilled constantly at 175—176°:

0·1142 gave 0·3706 CO_2 and 0·1248 H_2O. C=88·5; H=12·1.

$C_{10}H_{16}$ requires C=88·2; H=11·8 per cent.

0·9124, made up to 20 c.c. with ethyl acetate, gave α_D +2·71° in a 2-dcm. tube at 17°, whence $[\alpha]_D$ +29·6°.

l-1-*Methyl*-Δ^5-cyclo*hexene-3-carboxylic Acid*, l-Δ^5-m-*Menthenol*(8), *and* l-$\Delta^{5:8(9)}$-m-*Menthadiene.*

The mother liquors from the separation of the *l*-menthylamine and quinine salts of *d*-1-methyl*cyclo*hexene-3-carboxylic acid were decomposed in the usual manner, and the acid (60 grams), which distilled at 142—146° and had $[\alpha]_D$ −21·4°, was systematically treated with *l*-menthylamine and quinine, with the result that an acid was ultimately obtained which distilled at 142°/20 mm. and had the following rotation:

1·1009, made up to 20 c.c. in ethyl acetate, gave α_D −3·41° in a 2-dcm. tube at 15°, whence $[\alpha]_D$ −30·9°.

It follows therefore that this acid is nearly pure l-1-*methyl*-Δ^5-cyclo*hexene-3-carboxylic acid*, since the rotation of the corresponding *d*-acid was found to be +33·1°. Unfortunately no suitable crystalline salt of the *l*-acid was discovered, although experiments were made with *d*-bornylamine, *d*-*iso*menthylamine, and most of the usual alkaloids, and therefore complete separation could not be carried out.

Ethyl l-1-*Methyl*-Δ^5-cyclo*hexene*-3-*carboxylate*, prepared from the acid by means of alcoholic sulphuric acid in the usual manner, distilled at 140—142°/100 mm.:

1·0090, made up to 20 c.c. with ethyl acetate, gave α_D −2·78° in a 2-dcm. tube at 15°, whence $[\alpha]_D$ −27·4°.

This ester (27 grams) was added to an ethereal solution of magnesium methyl iodide containing 10 grams of magnesium, and, after remaining overnight, the product was decomposed by dilute hydrochloric acid in the usual manner, and yielded 22 grams of l-Δ^5-m-*menthenol*(8), which distilled at 104—105°/20 mm.:

0·1429 gave 0·4083 CO_2 and 0·1521 H_2O. C=77·7; H=11·8.

$C_{10}H_{18}O$ requires C=77·9; H=11·7 per cent.

0·9986, made up to 20 c.c. with ethyl acetate, gave α_D −32·5° in a 2-dcm. tube at 17°, whence $[\alpha]_D$ −32·6°.

The whole of this menthenol was boiled with dilute oxalic acid (6 per cent.) for three hours, the product distilled in a current of steam, and fractionated, first under ordinary conditions, and then twice over sodium; the l-$\Delta^{5:8(9)}$-m-*menthadiene* thus obtained distilled at 175—176°, and had a strong odour of lemons:

0·1056 gave 0·3414 CO_2 and 0·1135 H_2O. C=88·1; H=11·9.

$C_{10}H_{16}$ requires C=88·2; H=11·8 per cent.

1·0021, made up to 20 c.c. with ethyl acetate, gave α_D −2·58° in a 2-dcm. tube at 16°, whence $[\alpha]_D$ −25·3°.

Formation of the cis- *and* trans-*Lactones of* α-*Methyl*-γ-*hydroxy*-iso*propyladipic Acid by the Oxidation of* d- *and* l-Δ^5-m-*Menthenol*(8).

In carrying out this oxidation, *d*-Δ^5-*m*-menthenol(8) (5 grams) was suspended in water and powdered ice (1 litre), and then a 1 per cent. solution of permanganate (13 grams) added in several portions, the whole being mechanically shaken after each addition. The slight excess of permanganate was removed by sodium sulphite, and, after heating on the water-bath and filtering, the filtrate and washings of the manganese precipitate were evaporated to a small bulk. The brown liquid was then rendered acid with dilute sulphuric acid, and further oxidised on the water-bath with potassium dichromate and sulphuric acid until action ceased. The product was saturated with ammonium sulphate and repeatedly extracted with ether on the machine, the ethereal solution was dried and evaporated, and the syrupy residue esterified by boiling with 10 per cent. alcoholic sulphuric acid for twelve hours.

The ester was extracted with ether, the ethereal solution thoroughly washed with sodium carbonate, dried and evaporated, and the residue fractionated, when about two-thirds distilled at 188—190°/20 mm.:

0·1228 gave 0·2811 CO_2 and 0·0975 H_2O. C = 62·6; H = 8·8.

$C_{12}H_{20}O_4$ requires C = 63·2; H = 8·8 per cent.

1·0021, made up to 20 c.c. with alcohol, gave α_D −1·88° in a 2-dcm. tube at 17°, whence $[\alpha]_D$ −18·7°.

This ester was digested with dilute hydrochloric acid (3 per cent.) for several hours, evaporated to a small bulk, and the filtered liquid left over solid potassium hydroxide in a vacuum desiccator for some weeks, when the gummy mass gradually became semi-solid.

It was placed in contact with porous porcelain until quite colourless, and then several times crystallised from water, when a glistening mass of plates was obtained, which consisted of the *lactone* of trans-*α-methyl-γ-hydroxy*iso*propyladipic acid* * (compare p. 2132):

0·0907 gave 0·1999 CO_2 and 0·0657 H_2O. C = 60·1; H = 7·9.

$C_{10}H_{16}O_4$ requires C = 60·0; H = 8·0 per cent.

0·1888, dissolved in water and titrated with *N*/10-NaOH, neutralised 9·5 c.c., whereas this amount of a monobasic acid, $C_{10}H_{16}O_4$, should neutralise 9·4 c.c. A further 20·5 c.c. of *N*/10-NaOH (making 30 c.c. in all) were then added, the solution heated to boiling, and titrated back, when it was found that the total neutralised was 19·2 c.c. The amount required for neutralisation on the assumption that the lactone-acid, $C_{10}H_{16}O_4$, had become dibasic by hydrolysis is 18·8 c.c.

The solution was concentrated, acidified, heated to boiling for a few seconds, and allowed to cool; it then rapidly deposited glistening plates of the *trans*-lactone. This lactone melts at 136°, and is readily soluble in warm water, but rather sparingly so in the cold; the hot saturated solution clouds on cooling, but rapidly crystallises if the sides of the vessel are rubbed with a glass rod.

It is remarkable that, although obtained from a strongly active ester simply by boiling with dilute hydrochloric acid, this lactone, as also the corresponding *cis*-lactone (see below), should be quite inactive.

The cis-*Lactone.*—The porous plates, used in the purification of the crude mixed lactones, were extracted with ether, the ethereal extract mixed with water and the aqueous mother liquors of the *trans*-lactone, and digested with carefully purified animal charcoal. After filtering and evaporating to a small bulk, the solution was left over sulphuric acid, when it gradually deposited a mass of crystals, which were drained on porous porcelain and fractionally crystallised from water. In this way, a separation of the *trans*- and *cis*-lactones was ultimately accomplished.

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* This substance has been provisionally named *trans*- in order to distinguish it from the more readily soluble modification of lower melting point which has been called *cis*-.

The cis-*lactone* melts at about 102°, is readily soluble in warm water, and the concentrated solution clouds on cooling, as does that of the *trans*-lactone, and then deposits the lactone in glistening plates. On one occasion an aqueous solution, which had gradually concentrated in the air, deposited the *cis*-lactone in the form of a thick, glistening, prismatic crystal like a crystal of sugar. The analysis and titration of this lactone gave the following results:

0·1117 gave 0·2471 CO_2 and 0·0800 H_2O. C = 60·2; H = 8·0.

$C_{10}H_{16}O_4$ requires C = 60·0; H = 8·0 per cent.

0·2090, dissolved in water, neutralised 10·4 c.c. of *N*/10-NaOH, whereas this amount of a monobasic acid, $C_{10}H_{16}O_4$, should neutralise 10·45 c.c.

On boiling with an excess of sodium hydroxide and titrating back, it was found that 20·9 c.c. had been neutralised, which is exactly the amount the lactonic acid, after hydrolysis, should neutralise. The solution was concentrated, acidified, and boiled, when, on cooling, the lactone of melting point 102° crystallised out.

An exactly similar series of experiments were made on the oxidation of *l*-Δ^5-*m*-menthenol(8), and as they yielded a similar ester, $C_{12}H_{20}O_4$, of rotation $[\alpha]_D$ +17·4°, which, on hydrolysis, was converted into the inactive *cis*- and *trans*-lactones of melting points 102° and 136° respectively, it is hardly necessary to give the details of these experiments.

dl-1-*Methyl*-Δ^4-cyclo*hexene*-3-*carboxylic Acid*, dl-Δ^4-m-*Menthenol*(8), *and* dl-$\Delta^{4:8(9)}$-m-*Menthadiene*.

The calcium salt of 1-methyl-Δ^4-*m*-*cyclo*hexenecarboxylic acid, obtained as explained on p. 2138, was decomposed with dilute hydrochloric acid, the oily acid extracted with ether, the ethereal solution dried and evaporated, and the residual viscid oil distilled under diminished pressure, when the whole quantity passed over at 143—146°/20 mm.:

0·1256 gave 0·3159 CO_2 and 0·0991 H_2O. C = 68·5; H = 8·7.

$C_8H_{12}O_2$ requires C = 68·6; H = 8·6 per cent.

The constitution of this acid was proved by its conversion into 1-methyl-Δ^3-*cyclo*hexene-3-carboxylic acid when boiled with alkalis, an isomeric change which was brought about under the following conditions. The acid (8 grams) was digested with aqueous potassium hydroxide (50 c.c. of 30 per cent.) for four hours in a Jena-glass reflux apparatus, the solution was acidified, the acid extracted, dried, and left in contact with 30 c.c. of 8 per cent. alcoholic sulphuric acid at the ordinary temperature for fifteen hours. Water was then added, the oil extracted with ether, the ethereal solution washed with water, and then shaken with sodium carbonate in order to dissolve unesterified acid.* When the aqueous extract was acidified, an oily acid was deposited, which gradually crystallised, and this was collected and left in contact with porous porcelain until quite free from oil. The ester which had been produced yielded, on boiling with 30 per cent. potassium hydroxide and subsequent fractional esterification, a further quantity of the same solid (Δ^3) acid, and, when the operation was repeated a third time, a small quantity of solid acid was again obtained. Apparently a condition of equilibrium is established between the Δ^4- and Δ^3-acids during this process.

The solid acid was dissolved in sodium carbonate, digested with animal charcoal, again precipitated, and the colourless, crystalline mass, after remaining in contact with porous porcelain until quite dry, was analysed. Found, C = 68·6; H = 8·7. Calc., C = 68·6; H = 8·6 per cent.)

That this acid is 1-methyl-Δ^3-*cyclo*hexene-3-carboxylic acid was proved by the melting point, 58—60°, and by the fact that, when mixed with some of this acid, which had been prepared by Perkin and Tattersall (Trans., 1905, **87**, 1094) by another process, the mixture melted at the same temperature as the components. The identity was further proved by converting the acid into the dibromide (m. p. 165°) and hydrobromide (m. p. 108—109°; compare this vol., p. 2152).

Ethyl 1-*Methyl*-Δ^4-cyclo*hexene*-3-*carboxylate*.—This ester was prepared by digesting the acid (10 grams) with 6 per cent. alcoholic sulphuric acid (50 c.c.) for three hours, and, after the addition of water, extracting with ether in the usual way. It distilled at 142—144°/100 mm., and had a most unpleasant and penetrating odour.

This ester (10 grams) was added to an ethereal solution of magnesium methyl iodide, containing 4 grams of magnesium, and, after remaining for twenty-four hours, water was added and the product distilled in a current of steam. The distillate was extracted with ether, the ethereal solution dried and evaporated, and the Δ^4-m-*menthenol*(8) distilled under diminished pressure, when it passed over at 115—117°/30 mm. as a viscid oil which had a strong odour of terpineol and menthol:

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* This method of separation depends on the fact that 1-methyl-Δ^3-*cyclo*hexenecarboxylic acid is an $\alpha\beta$-unsaturated acid, and is esterified with greater difficulty than 1-methyl-Δ^4-*cyclo*hexenecarboxylic acid, which contains the ethylene linking in the $\beta\gamma$-position. The value of this process of separation will be discussed in detail in a subsequent communication.

0·1145 gave 0·3267 CO_2 and 0·1224 H_2O. C = 77·8; H = 11·9.
$C_{10}H_{18}O$ requires C = 77·9; H = 11·7 per cent.

$\Delta^{4:8(9)}$-m-*Menthadiene* was obtained from Δ^4-*m*-menthenol(8) by boiling with 6 per cent. aqueous oxalic acid exactly as described in the preparation of $\Delta^{5:8(9)}$-*m*-menthadiene (p. 2139). It was purified by distillation in a current of steam and then twice over sodium, and boiled at 175—177°/757 mm.:

0·1347 gave 0·3358 CO_2 and 0·1452 H_2O. C = 88·2; H = 11·9.
$C_{10}H_{16}$ requires C = 88·2; H = 11·8 per cent.

The amount of these substances available was very small, and an attempt will be made to find a more satisfactory method for the preparation of 1-methyl-Δ^4-*cyclo*hexene-3-carboxylic acid in order, if possible, to prepare the active menthenols and menthadienes derived from it.

The author is indebted to Dr. A. N. Meldrum and Mr. L. Benson for preparing the 1-methyl*cyclo*hexan-5-ol-3-carboxylic acid required for this investigation, and to Miss B. Dobson for carrying out most of the analyses and determinations of refractive power.

The author also wishes to state that much of the heavy expense of this research was met by a grant from the Research Fund of the Royal Society.

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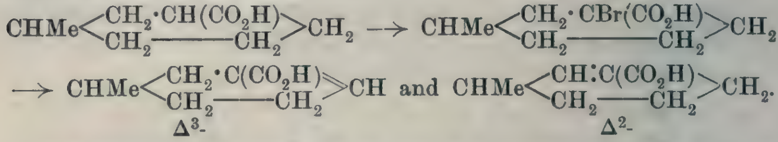
CCXXIV.—*Experiments on the Synthesis of the Terpenes. Part XV.* Δ^3-m-*Menthenol*(8) *and* $\Delta^{3:8(9)}$-m-*Menthadiene.*

By BERNARD DUNSTAN WILKINSON LUFF (1851 Exhibition Scholar) and WILLIAM HENRY PERKIN, jun.

IN a previous communication (Trans., 1905, **87**, 1085), it was shown that 1-methyl*cyclo*hexan-3-carboxylic acid (hexahydro-*m*-toluic acid) is readily converted by bromination and subsequent elimination of hydrogen bromide into a mixture of 1-methyl-Δ^3- and -Δ^2-*cyclo*hexene-3-carboxylic acids:

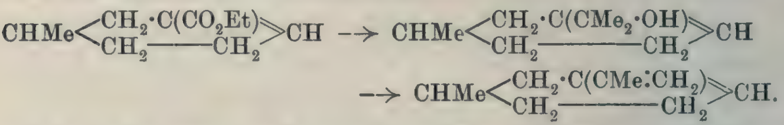


$$\mathrm{CHMe}\left\langle\begin{array}{l}\mathrm{CH_2\cdot CH(CO_2H)}\\ \mathrm{CH_2{-}{-}{-}{-}CH_2}\end{array}\right\rangle\mathrm{CH_2} \longrightarrow \mathrm{CHMe}\left\langle\begin{array}{l}\mathrm{CH_2\cdot CBr(CO_2H)}\\ \mathrm{CH_2{-}{-}{-}{-}CH_2}\end{array}\right\rangle\mathrm{CH_2}$$

$$\longrightarrow \underset{\Delta^{3}\text{-}}{\mathrm{CHMe}\left\langle\begin{array}{l}\mathrm{CH_2\cdot C(CO_2H)}\\ \mathrm{CH_2{-}{-}{-}CH_2}\end{array}\right\rangle\mathrm{CH}} \text{ and } \underset{\Delta^{2}\text{-}}{\mathrm{CHMe}\left\langle\begin{array}{l}\mathrm{CH{:}C(CO_2H)}\\ \mathrm{CH_2{-}{-}{-}CH_2}\end{array}\right\rangle\mathrm{CH_2}}.$$

The separation of acids of such similar constitution proved to be a matter of much difficulty, and, as a result, only small quantities of the pure isomerides were available for subsequent investigation.

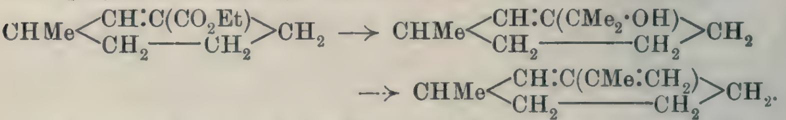
1-Methyl-Δ^3-*cyclo*hexene-3-carboxylic acid (m. p. 58—60°) was converted into its ester, and this, by the action of magnesium methyl iodide, into Δ^3-*m*-menthenol(8), a substance which, when left in contact with a large excess of magnesium methyl iodide, loses water with formation of $\Delta^{3:8(9)}$-*m*-menthadiene:



$$\mathrm{CHMe}\left\langle\begin{array}{l}\mathrm{CH_2\cdot C(CO_2Et)}\\ \mathrm{CH_2{-}{-}{-}CH_2}\end{array}\right\rangle\mathrm{CH} \longrightarrow \mathrm{CHMe}\left\langle\begin{array}{l}\mathrm{CH_2\cdot C(CMe_2\cdot OH)}\\ \mathrm{CH_2{-}{-}{-}{-}CH_2}\end{array}\right\rangle\mathrm{CH}$$

$$\longrightarrow \mathrm{CHMe}\left\langle\begin{array}{l}\mathrm{CH_2\cdot C(CMe{:}CH_2)}\\ \mathrm{CH_2{-}{-}{-}{-}CH_2}\end{array}\right\rangle\mathrm{CH}.$$

In a similar manner, Δ^2-*m*-menthenol(8) and $\Delta^{2:8(9)}$-*m*-menthadiene were prepared from ethyl 1-methyl-Δ^2-*cyclo*hexene-3-carboxylate:

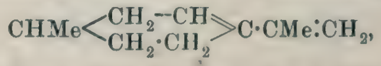


$$\mathrm{CHMe}\left\langle\begin{array}{l}\mathrm{CH{:}C(CO_2Et)}\\ \mathrm{CH_2{-}{-}CH_2}\end{array}\right\rangle\mathrm{CH_2} \longrightarrow \mathrm{CHMe}\left\langle\begin{array}{l}\mathrm{CH{:}C(CMe_2\cdot OH)}\\ \mathrm{CH_2{-}{-}{-}{-}CH_2}\end{array}\right\rangle\mathrm{CH_2}$$

$$\longrightarrow \mathrm{CHMe}\left\langle\begin{array}{l}\mathrm{CH{:}C(CMe{:}CH_2)}\\ \mathrm{CH_2{-}{-}{-}{-}CH_2}\end{array}\right\rangle\mathrm{CH_2}.$$

It will be observed that $\Delta^{3:8(9)}$- and $\Delta^{2:8(9)}$-*m*-menthadiene contain conjugated double linkings, and investigation showed that these terpenes do, in fact, show the characteristic behaviour of substances which contain such groupings; they are, for example, only able to combine with two atoms of bromine or with one molecule of hydrogen chloride (compare Trans., 1905, **87**, 641, 667, and 1068).

A short time since (this vol., p. 1428), Perkin and Wallach made a special study of another synthetical terpene which contains conjugated double linkings, namely, $\Delta^{3:8(9)}$-*p*-methadiene:

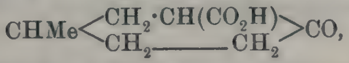


$$\mathrm{CHMe}\left\langle\begin{array}{l}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2\cdot CH_2}\end{array}\right\rangle\mathrm{C\cdot CMe{:}CH_2},$$

and observed that this terpene had a higher boiling point, density, and refractive index than terpenes, such as limonene, which do not contain conjugated double linkings (compare p. 2154), and it seemed desirable to investigate the physical constants of other terpenes of similar structure in order to determine whether this behaviour is a general one. The difficulty in preparing the *m*-menthadienes already mentioned in amount sufficient for accurate physical measurement is due to the difficulty in obtaining the 1-methyl-

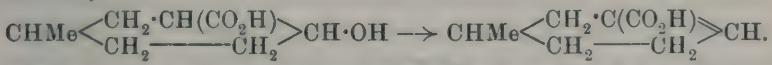
*cyclo*hexene-3-carboxylic acids in any considerable quantity by the process described at the beginning of this paper. An attempt was therefore made to devise a new method for the preparation of these acids, and this has been successful in the case of the Δ^3-acid (m. p. 58—60°).

Quite recently (this vol., p. 1760), it was pointed out that 1-methyl*cyclo*hexan-4-one reacts readily with sodamide and carbon dioxide, with the formation of 1-methyl*cyclo*hexan-4-one-3-carboxylic acid:



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CH(CO_2H)}\\ \mathrm{CH_2}\text{———}\mathrm{CH_2}\end{matrix}>\mathrm{CO},$$

and we have found that, under the conditions described in the present communication (p. 2150), the yield directly obtained is 50 per cent. of that theoretically possible.* When this acid is reduced with sodium amalgam, it yields 1-methyl*cyclo*hexan-4-ol-3-carboxylic acid, and this, on distillation, is almost quantitatively converted into 1-methyl-Δ^3-*cyclo*hexene-3-carboxylic acid (m. p. 58—60°):



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CH(CO_2H)}\\ \mathrm{CH_2}\text{———}\mathrm{CH_2}\end{matrix}>\mathrm{CH\cdot OH}\longrightarrow\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot C(CO_2H)}\\ \mathrm{CH_2}\text{——}\mathrm{CH_2}\end{matrix}\geqslant\mathrm{CH}.$$

This method of preparation is still laborious, but it is much less so than the original method, and it has now been found possible to prepare nearly 200 grams of the pure acid, of which part has been used in the present research, and the remainder is being resolved into its active constituents with the object of preparing and carefully investigating the corresponding active menthenols and menthadienes. In possession of sufficient material, we have now very carefully determined the physical properties of Δ^3-*m*-menthenol(8) and $\Delta^{3:8(9)}$-*m*-menthadiene (see pp. 2153, 2154).

We find that the values of Δ^3-*m*-menthenol(8) show a remarkable similarity to those of Δ^3-*p*-menthenol(8), and, when these numbers are compared with those of terpineol, it is seen that the proximity of the double linking to the $\cdot\mathrm{CMe_2\cdot OH}$ group causes a fall of boiling point, density, and refractive index. Similarly, the values for $\Delta^{3:8(9)}$-*m*-menthadiene are very like those of $\Delta^{3:8(9)}$-*p*-menthadiene, but, when these values are compared with those of limonene, it is seen that the presence of conjugated linkings causes a considerable rise in boiling point, density, and refractive index.

A similar study of Δ^2-*m*-menthenol(8) and of $\Delta^{2:8(9)}$-*m*-menthadiene is in progress, and the results will shortly be ready for publication.

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* It is actually considerably more, because a good deal of ketone is recovered unchanged and may be employed in a subsequent preparation.

EXPERIMENTAL.

Preparation of 1-*Methyl*cyclo*hexan*-4-*one*-3-*carboxylic Acid and* 1-*Methyl*cyclo*hexan*-4-*ol*-3-*carboxylic Acid.*

In order to obtain the large quantities of the above ketonic acid which we required for this research, we decided, as the result of a long series of comparative experiments, to modify the method of preparation originally employed (this vol., p. 1766) in the following way.

1-Methyl*cyclo*hexan-4-one (100 grams) is dissolved in dry ether (1 litre) in a three-necked flask fitted with a reflux condenser and mechanical stirrer, powdered sodamide (40 grams) is then added in lots of 10 grams, and the stirrer set in motion, when a rapid evolution of ammonia takes place. After the reaction has subsided, the mixture is heated on the steam-bath for an hour, allowed to cool, and then a stream of dry carbon dioxide passed through a wide tube so as to avoid stoppage, the whole being vigorously stirred during the operation. This causes a rise of temperature, and the passage of the gas is continued until the whole has cooled down to that of the atmosphere. The contents of the flask are then washed into a separating funnel with ice water, well agitated, the aqueous layer run off, and the ethereal solution kept in order to recover the unchanged ketone which it contains. The aqueous solution is acidified, extracted with ether, the ethereal solution shaken with sodium carbonate, and, after separating, the alkaline extract is cautiously treated with hydrochloric acid until the oily impurity has been completely precipitated and the crystalline acid commences to separate. After filtering, the filtrate is acidified with hydrochloric acid, and the colourless, crystalline precipitate of nearly pure 1-methyl*cyclo*hexan-4-one-3-carboxylic acid collected, washed, and drained on porous porcelain. The yield is 45—50 grams. The ethereal layer, containing the unchanged ketone, is washed, evaporated, and the residue distilled in a current of steam in order to separate it from a quantity of the bicyclic condensation product described on p. 2155. The ketone is extracted from the distillate, and, after one fractionation, is sufficiently pure for a further operation.

In preparing 1-methyl*cyclo*hexan-4-ol-3-carboxylic acid, 1-methyl*cyclo*hexan-4-one-3-carboxylic acid, in quantities of 10 grams, is dissolved in sodium carbonate, the solution made up to 600 c.c. with water, and treated, in a bottle fitted with a mechanical stirrer, with freshly prepared sodium amalgam (500 grams), which is added in three lots. Reduction takes place very slowly at the ordinary temperature, and the most suitable temperature appears to be

50—60°, which is maintained during the whole operation by placing the bottle in a trough of hot water; it is also necessary to neutralise the alkali produced by hydrochloric acid, which is dropped in in such a way that the liquid is always faintly alkaline.

The product is acidified with hydrochloric acid, saturated with salt, and extracted at least five times with much ether; the ethereal extract is dried over anhydrous sodium sulphate, and evaporated, when a syrup remains which soon becomes semi-solid, and the purification and properties of which have already been described (this vol., p. 1770).

1-*Methyl*-Δ^3-cyclo*hexene*-3-*carboxylic Acid.*

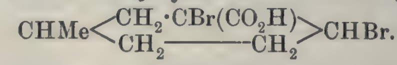
This acid has been prepared in large quantities in the following manner. Crude 1-methyl*cyclo*hexan-4-ol-3-carboxylic acid, obtained as described in the last section, is transferred to a distilling flask with a rather long neck, and heated in a metal-bath, when effervescence soon occurs, due to the decomposition of some unchanged ketonic acid. In a short time, water commences to be eliminated, and as soon as this and the ketone have ceased to pass over, the residue is distilled under diminished pressure, when almost the whole passes over at 155—160°/25 mm., and solidifies on cooling. The mass is left in contact with porous porcelain until free from traces of oily impurity; it then melts at about 57—58°, and is almost pure 1-methyl-Δ^3-*cyclo*hexene-3-carboxylic acid. The yield is approximately 10 grams from 50 grams of the crude hydroxy-acid. For analysis, the substance was crystallised from formic acid, from which it separates in pearly plates, melting at 60°. (Found, $C=68{\cdot}4$; $H=8{\cdot}6$. Calc., $C=68{\cdot}6$; $H=8{\cdot}6$ per cent.)

Careful comparison has shown that this acid is identical with the "Δ^1-tetrahydro-*m*-toluic acid" obtained by Perkin and Tattersall (Trans., 1905, **87**, 1092) by quite a different process. Ethyl 1-methyl-Δ^3-*cyclo*hexene-3-carboxylate, which has already been described (*loc. cit.*, p. 1094), was prepared in quantity by leaving the pure acid (50 grams) in contact with alcohol (300 c.c.) and sulphuric acid (30 c.c.) at the ordinary temperature for two days, and then heating on the water-bath for two hours.

After extracting in the usual way, it distilled at 146—148°/100 mm.

It was noticed that the $\alpha\beta$-unsaturated acid is esterified with some difficulty at the ordinary temperature. Thus, for example, the mixture just mentioned, after being kept for twenty-four hours, contained a large amount of acid, and, even after forty-eight hours, a considerable quantity of unesterified acid was still present. This behaviour has been utilised for separating the acid from the isomeric βγ-acid by a process of fractional esterification (compare this vol., p. 2146).

3 : 4-*Dibromo*-1-*methyl*cyclo*hexane*-3-*carboxylic Acid*,



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CBr(CO_2H)}\\ \mathrm{CH_2}\text{———}\mathrm{CH_2}\end{matrix}>\mathrm{CHBr}.$$

In order to prepare this characteristic derivative, pure 1-methyl-Δ^3-*cyclo*hexene-3-carboxylic acid, dissolved in a little dry chloroform, is cooled to −5°, and mixed with a few drops of dry bromine. At this low temperature, no action seems to take place, but, if allowed to rise to 15°, the colour of the bromine suddenly disappears, and then the addition of the theoretical amount takes place rapidly at 0°. During the operation a good deal of the dibromo-acid crystallises out, and the remainder is obtained by allowing the chloroform to evaporate. It is sparingly soluble in cold formic acid, and not very readily so on boiling, and separates in colourless, glistening leaflets:

0·3166 gave 0·3945 AgBr. Br = 53·0.

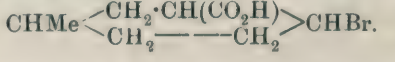
$C_8H_{12}O_2Br_2$ requires Br = 53·3 per cent.

When rapidly heated, 3 : 4-dibromo-1-methyl*cyclo*hexane-3-carboxylic acid melts at 165°.

It dissolves readily in sodium carbonate, and the solution, on boiling, does not cloud with separation of the bromohydrocarbon, as sometimes happens in the case of αβ-dibromo-acids of similar constitution. After boiling for ten minutes with a large excess of sodium carbonate, the solution deposited, on acidifying, a solid acid, which crystallised well from formic acid, melted at 148—150°, and appears to be a bromohydroxy-acid of the formula $C_7H_{11}Br(OH)\cdot CO_2H$ (Found, Br = 32·7. Calc., Br = 33·2), but it was not further investigated.

The aqueous filtrate from this acid contains a considerable quantity of a syrupy acid which may be extracted with ether, and is probably the corresponding dihydroxy-acid.

4-*Bromo*-1-*methyl*cyclo*hexane*-3-*carboxylic Acid*,



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CH(CO_2H)}\\ \mathrm{CH_2}\text{———}\mathrm{CH_2}\end{matrix}>\mathrm{CHBr}.$$

1-Methyl-Δ^3-*cyclo*hexene-3-carboxylic acid dissolves readily in fuming hydrobromic acid (saturated at 0°), and, on keeping, but more rapidly if slowly warmed to 70°, a syrup separates, which gradually crystallises. After washing with water and draining on porous porcelain, the substance was dissolved in a little warm formic acid, in which it is very readily soluble, and from which it separates in needles, melting at 107—109°:

0·1544 gave 0·1314 AgBr. Br = 36·2.

$C_8H_{13}O_2Br$ requires Br = 36·2 per cent.

This bromo-acid is decomposed by boiling with sodium carbonate, and the solution, on acidifying, deposits a crystalline precipitate of 1-methyl-Δ^3-*cyclo*hexene-3-carboxylic acid.

Δ^3-m-*Menthenol*(8) *and* $\Delta^{3:8(9)}$-m-*Menthadiene.*

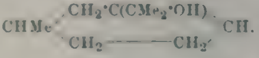
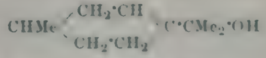
The conversion of ethyl 1-methyl-Δ^3-*cyclo*hexen-3-carboxylate into Δ^3-*m*-menthenol(8) was carried out by adding the ester (13 grams) to an ethereal solution of magnesium methyl iodide, containing 6·5 grams of magnesium. After fifty hours, the product was decomposed by *water* (compare footnote, p. 2154), distilled in a current of steam, the distillate extracted with ether, and the ethereal solution dried, evaporated, and the residue distilled under diminished pressure. The whole quantity passed over at 114—117°/35 mm., and, after redistillation at 115°/35 mm., as a colourless, pleasant smelling, rather viscid liquid, and the yield of this pure Δ^3-*m*-menthenol(8) was almost quantitative. The first time this substance was prepared (Trans., 1905, **87**, 1100), it was noticed that much of the ethyl ester remained unattacked; this was due to the fact that the amount of magnesium (2·9 grams to 10 grams of ester) was too small, and the length of contact (twenty-four hours) was also not sufficient. Under the conditions mentioned above, only a trace of ethyl ester remained unchanged, and this was removed, before fractionation, by hydrolysis with a little methyl-alcoholic potassium hydroxide in the usual manner.

The *phenylurethane* of Δ^3-*m*-menthenol(8) was prepared by leaving the menthenol with an equal volume of phenylcarbimide for three days. The mass was drained on porous porcelain, and then crystallised from 80 per cent. methyl alcohol, from which it separated in colourless needles, melting at 130°:

0·1057 gave 5·0 c.c. N_2 at 21° and 758 mm. N = 5·3.

$C_{17}H_{23}O_2N$ requires N = 5·1 per cent.

The physical properties of Δ^3-*m*-menthenol(8) have been carefully determined, and found to be very similar to those of Δ^3-*p*-menthenol(8) (compare Perkin and Wallach, this vol., p. 1435), as the following comparison shows:

	 $\mathrm{CHMe}\begin{matrix}\diagup\mathrm{CH_2{\cdot}C(CMe_2{\cdot}OH)}\diagdown\\ \diagdown\mathrm{CH_2\text{———}CH_2}\diagup\end{matrix}\mathrm{CH.}$	 $\mathrm{CHMe}\begin{matrix}\diagup\mathrm{CH_2{\cdot}CH}\diagdown\\ \diagdown\mathrm{CH_2{\cdot}CH_2}\diagup\end{matrix}\mathrm{C{\cdot}CMe_2{\cdot}OH}$
B p.	102°/14 mm.	115°/35 mm.
d. 20°/20°	0·9268	0·9210
n_D	1·4798	1·4768
M.	47·10 (calc. 47·16)	47·23
M. p. of the phenylurethane	130°	128°

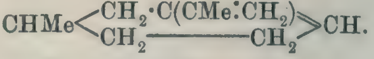
Δ^3-*m*-Menthenol(8) has, so far, not crystallised, whereas Δ^3-*p*-menthenol(8) is solid, and melts at 39°.

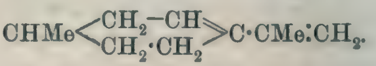
$\Delta^{3:8(9)}$-*m*-Menthadiene has been prepared in two different ways, namely, (1) by the direct action of magnesium methyl iodide on ethyl 1-methyl-Δ^3-*cyclo*hexene-3-carboxylate, and (2) by the action of aqueous oxalic acid on Δ^3-*m*-menthenol(8).

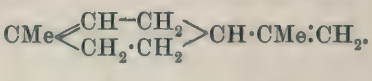
1. Ethyl 1-methyl-Δ^3-*cyclo*hexene-3-carboxylate (25 grams) was added to an ethereal solution of magnesium methyl iodide (10 grams of magnesium), and, after forty-eight hours, the product was decomposed by *dilute hydrochloric acid* * and distilled in a current of steam. The ethereal extract of the distillate was dried, evaporated, and the product fractionated, when almost the whole passed over at 178—183°/750 mm., the amount of Δ^3-*m*-menthenol remaining being very small.

The $\Delta^{3:8(9)}$-*m*-menthadiene was then distilled three times over sodium, when it boiled constantly at 181—182°/760 mm.

2. Δ^3-*m*-Menthenol(8) was boiled for three hours with 6 per cent. aqueous oxalic acid, and the product distilled in a current of steam. After extracting in the usual manner, it was found that the conversion into $\Delta^{3:8(9)}$-*m*-menthadiene had been almost quantitative, and that this terpene again distilled at 181—182°/760 mm. The physical properties of both the specimens of this terpene were carefully determined, and found to be practically identical, and it is interesting to tabulate these (I) with those of the two following terpenes:

I. $\Delta^{3:8(9)}$-*m*-Menthadiene, 
$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot C(CMe{:}CH_2)}\\ \mathrm{CH_2\text{———}CH_2}\end{matrix}>\mathrm{CH}.$

II. $\Delta^{3:8(9)}$-*p*-Menthadiene, 
$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C\cdot CMe{:}CH_2}.$

III. Limonene, 
$\mathrm{CMe}<\begin{matrix}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH\cdot CMe{:}CH_2}.$

	I.	II.	III.
B. p.	181—182°	184—185°	175—176°
d. 20°/20°	0·8609	0·8580	0·8460
n_D	1·4975	1·4924	1·4746
M.	46·3	46·02	45·23

$(C_{10}H_{16}|^{=2} = 45{\cdot}24.)$

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* The curious observation (compare p. 2153) has been made in this and in other cases, that the product of the action of magnesium methyl iodide on the ester of a methyl*cyclo*hexenecarboxylic acid, containing the double linking in the $\alpha\beta$-position, yields the menthenol when it is treated with *water*, but the conjugated menthadiene when it is decomposed by *dilute hydrochloric acid*. In cases where the double linking is in any other position, this difference has not been observed, and the product has always been the menthenol whether the decomposition has been carried out simply by water or by the addition of hydrochloric acid.

Cases I and II prove again that the effect of conjugation is to raise the boiling point, density, and refractive index above those of limonene. In possession of considerable quantities of pure $\Delta^{3:8(9)}$-*m*-menthadiene, the authors have again investigated its behaviour with bromine and with hydrogen chloride (compare Trans., 1905, **87**, 1101). The freshly distilled terpene (3·3588 grams) was dissolved in twice its volume of chloroform, cooled to −15°, and titrated with a solution of bromine in chloroform (1 in 3), when 12·6 c.c. were decolorised, the end-point being quite sharp, but a little hydrogen bromide was produced. This amount of terpene had therefore decolorised 4·2 grams of bromine, whereas the amount required for the formation of the tetrabromide, $C_{10}H_{16}Br_4$, is 8·0, and for the dibromide, $C_{10}H_{16}Br_2$, 4·0 grams. It is clear therefore, as had previously been pointed out, that this and other conjugated terpenes are only capable of combining with two atoms of bromine.

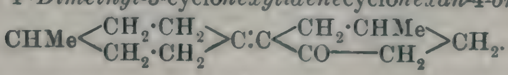
In investigating the action of hydrogen chloride, about 5 c.c. of the terpene were cooled to −15°, and a current of dry hydrogen chloride passed for one hour; the almost colourless product was left for two days, then placed over potassium hydroxide in a vacuum desiccator for several hours, and analysed:

0·1773 gave 0·1390 AgCl. $Cl = 19·4$.

$C_{10}H_{16},HCl$ requires $Cl = 20·6$ per cent.

It is therefore obvious that this conjugated menthadiene is only capable of combining with one molecule of hydrogen chloride.

1 : *4′-Dimethyl*-3-cyclo*hexylidene*cyclo*hexan*-4-*one*,



$$CHMe{<}\substack{CH_2\cdot CH_2\\ CH_2\cdot CH_2}{>}C{:}C{<}\substack{CH_2\cdot CHMe\\ CO\text{——}CH_2}{>}CH_2.$$

Considerable quantities of this ketone, as well as higher condensation products of 1-methyl*cyclo*hexan-4-one, are produced during the action of sodamide and carbon dioxide (p. 2150). After extracting the sodium salt of 1-methyl*cyclo*hexan-4-one-3-carboxylic acid with water, the ethereal solution is evaporated, and the residue distilled in a current of steam, when unchanged methyl*cyclo*hexanone passes over, and the condensation products remain in the distilling flask. The dark brown oil is extracted with ether, the ethereal solution dried and evaporated, and the residue fractionated under diminished pressure, when a quantity of a pale yellow oil is obtained, which distils at 173—174°/25 mm., and has a pronounced fruity odour:

0·1971 gave 0·5862 CO_2 and 0·1924 H_2O. $C = 81·1$; $H = 10·8$.

$C_{14}H_{22}O$ requires $C = 81·5$; $H = 10·7$ per cent.

d 20°/20° = 0·9728; $n = 1·4986$; $M = 62·1$ (calc., 62·4).

This condensation product is very similar to the "bicyclic ketone," $C_{14}H_{22}O$, which Wallach (*Ber.*, 1896, **29**, 1595) obtained by the action of hydrogen chloride on 1-methyl*cyclo*hexan-3-one.

When a drop of sulphuric acid is added to the solution of the ketone in acetic anhydride, an intense crimson coloration is produced, which persists for a long time. The *oxime* was obtained by adding an aqueous solution of hydroxylamine hydrochloride to an alcoholic solution of the ketone, when, almost immediately, a crystalline precipitate began to form, which, after crystallisation from alcohol, was obtained in glistening needles, melting at 160°:

0·463 gave 26·4 c.c. N_2 at 18° and 758 mm. N = 6·7.

$C_{14}H_{23}ON$ requires N = 6·3 per cent.

THE UNIVERSITY,
MANCHESTER.

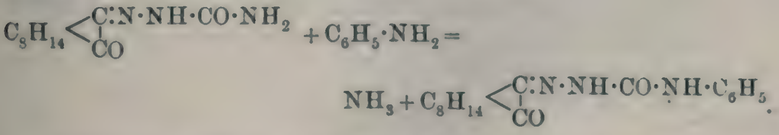
CCXXV.—*Studies in the Camphane Series. Part XXVIII. Stereoisomeric Hydrazones and Semicarbazones of Camphorquinone.*

By MARTIN ONSLOW FORSTER and ADOLF ZIMMERLI.

THE expectation of stereoisomerism among semicarbazones is a natural corollary of the Hantzsch-Werner hypothesis. Up to the present time, however, it does not appear that any systematic attempt has been made to place the question of semicarbazone-isomerism on the basis occupied by that of the oximes. Apart from the distrust with which the hypothesis in question is still viewed in some quarters, the principal reason for this omission to bring the semicarbazones into line with oximes is the scattered and ill-defined nature of the evidence relating to the occurrence of isomerism in the former class. The cases of *iso*thujone, carvenone, and tetrahydrocarvone appear to have been established by Wallach (*Ber.*, 1895, **28**, 1955), but the isomeric semicarbazones of citral and of ionone owe their formation to the existence of each ketone in two isomeric forms. Wallach has also shown that synthetical pulegone, obtained by condensation of methylhexanone with acetone, yields two semicarbazones (*Ber.*, 1896, **29**, 2955 also *Annalen*, 1898, **300**, 269), from both of which the ketone is regenerated by acid, but a claim for the production of isomerides from phenyl-1-methyl-Δ^6-*cyclo*hexen-5-one (Knoevenagel and Gold-smith, *Ber.*, 1898, **31**, 2465) is not based on strong evidence. Benzoylmethylthiodiazole, on the other hand, gives rise to two derivatives (Wolff, *Annalen*, 1902, **325**, 173), but the supposed existence of two benzilmonosemicarbazones (Posner, *Ber.*, 1901, **34**, 3979) was shown to be fallacious by Biltz and Arnd (*Ber.*, 1902, **35**, 344; compare also Biltz, *Annalen*, 1905, **339**, 243), the second substance being 5 : 6-diphenyl-3-oxy-1 : 2 : 4-triazine, prepared by Thiele and Stange (*Annalen*, 1894, **283**, 27). Nef has recorded the production of two semicarbazones from propaldehyde (*Annalen*, 1904, **335**, 202), whilst Knoevenagel and Samel (*Ber.*, 1906, **39**, 681), and later Rupe and Dorschky (*Ber.*, 1906, **39**, 2112), found that when semicarbazide acts on carvone in the cold, the product is distinct from that described by von Baeyer, into which, however, it is convertible at raised temperatures.

In reviewing the foregoing evidence relating to the existence of isomeric semicarbazones, we have not encountered any systematic attempt to explain the phenomenon, but the experiments described in this paper lead us to express the opinion that stereoisomerism of the type displayed by oximes must now be regarded as existing in this class also.

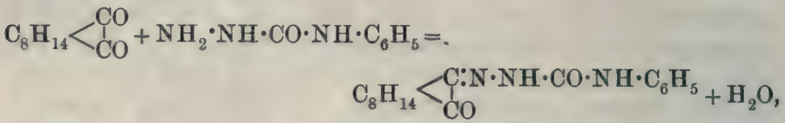
Our attention was drawn to the subject by an observation made in connexion with camphorquinonesemicarbazone (Lapworth and Chapman, Trans., 1901, **79**, 381), and our thanks are due to Dr. Lapworth for his consent to our using this material. In preparing it by the slightly modified process of Diels and vom Dorp (*Ber.*, 1903, **36**, 3190), we noticed that the mother liquor contained a more soluble isomeride melting at a lower temperature than the modification already described, and calling the latter the α-derivative, we refer to the new compound as the β-semicarbazone. When this is heated above its melting point, it is converted into the α-semicarbazone, and the latter, under the influence of hot aniline, undergoes the change described by Borsche (*Ber.*, 1901, **34**, 4297; 1904, **37**, 3177), giving rise to camphorquinonephenylcarbamylhydrazone, with liberation of ammonia:



$$C_8H_{14}<\begin{matrix}C:N\cdot NH\cdot CO\cdot NH_2\\ | \\ CO\end{matrix} + C_6H_5\cdot NH_2 =$$

$$NH_3 + C_8H_{14}<\begin{matrix}C:N\cdot NH\cdot CO\cdot NH\cdot C_6H_5\\ | \\ CO\end{matrix}.$$

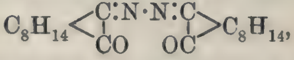
The product, however, is an equilibrium mixture of two isomerides, related to one another in a manner similar to the connexion between the semicarbazones. Both camphorquinonephenylcarbamylhydrazones are produced, also, when the β-semicarbazone is heated with aniline, and by the condensation of camphorquinone with phenylcarbamylhydrazide:



$$C_8H_{14}<\begin{matrix}CO\\|\\CO\end{matrix} + NH_2\cdot NH\cdot CO\cdot NH\cdot C_6H_5 = C_8H_{14}<\begin{matrix}C{:}N\cdot NH\cdot CO\cdot NH\cdot C_6H_5\\|\\CO\end{matrix} + H_2O,$$

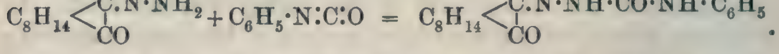
and they may be obtained separately by the action of phenylcarbimide on two new hydrazones of camphorquinone.

The action of hydrazine on camphorquinone is stated by Oddo (*Gazzetta*, 1897, **27**, ii, 117) to yield "biscamphanonazine," identical with Angeli's azocamphanone (*Gazzetta*, 1894, **24**, ii, 44), produced in association with camphenone by heating diazocamphor. As represented by Angeli, the formation of azocamphanone:



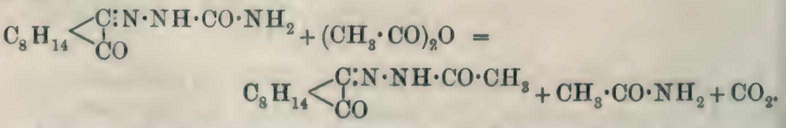
$$C_8H_{14}<\begin{matrix}C{:}N\cdot N{:}C\\|\qquad\quad|\\CO\quad\ OC\end{matrix}>C_8H_{14},$$

obviously depends on the condensation of hydrazine with two molecules of the diketone, but we find that if the substances interact in molecular proportion, two new derivatives of camphorquinone are produced; these, being isomeric, are referred to as the α- and β-hydrazones, and it is by the action of phenylcarbimide on these two substances that the above-mentioned α- and β-phenylcarbamylhydrazones are respectively obtainable:



$$C_8H_{14}<\begin{matrix}C{:}N\cdot NH_2\\|\\CO\end{matrix} + C_6H_5\cdot N{:}C{:}O = C_8H_{14}<\begin{matrix}C{:}N\cdot NH\cdot CO\cdot NH\cdot C_6H_5\\|\\CO\end{matrix}.$$

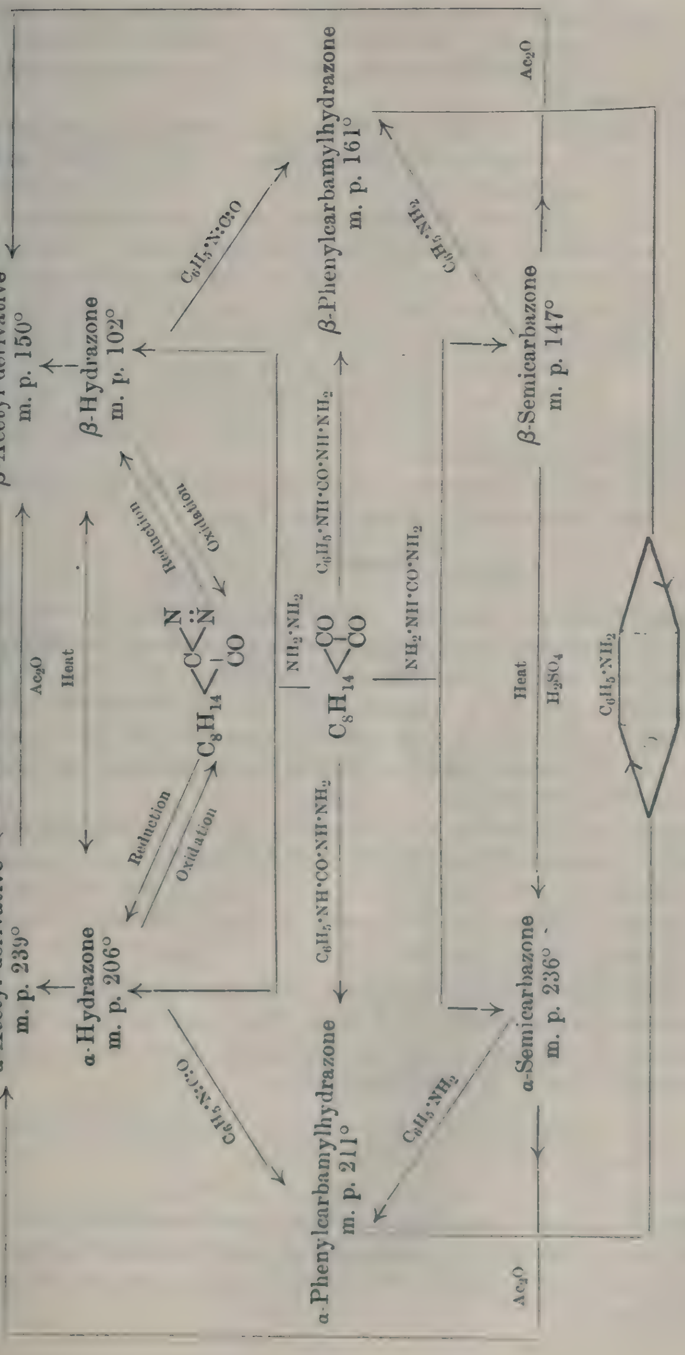
Thus, the isomeric hydrazones (m. p. 206° and 102°) are connected through the isomeric phenylcarbamylhydrazones (m. p. 211° and 161°) with the isomeric semicarbazones (m. p. 236° and 147°) respectively, and the members of each pair bear to one another the same relation in respect of solubility, fusibility, and interconvertibility by heat. A further connexion between the hydrazones and semicarbazones is established by the fact that whilst acetic anhydride converts the hydrazones into acetyl derivatives (m. p. 239° and 150°), of which the β-compound is transformed into the α-modification by heat, an equilibrium mixture of these isomeric acetyl derivatives follows the action of hot acetic anhydride on the isomeric semicarbazones:



$$C_8H_{14}<\begin{matrix}C{:}N\cdot NH\cdot CO\cdot NH_2\\|\\CO\end{matrix} + (CH_3\cdot CO)_2O = C_8H_{14}<\begin{matrix}C{:}N\cdot NH\cdot CO\cdot CH_3\\|\\CO\end{matrix} + CH_3\cdot CO\cdot NH_2 + CO_2.$$

These reactions are summarised in the diagram on p. 2159.

It now becomes necessary to explain our grounds for ascribing the present case of isomerism to stereochemical rather than struc-

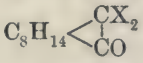

α-Acetyl derivative m. p. 239°
β-Acetyl derivative m. p. 150°
α-Hydrazone m. p. 206°
β-Hydrazone m. p. 102°
Heat
Ac₂O
Heat
Reduction
Oxidation
Reduction
Oxidation
C₈H₁₄<C:N:N / CO
C₈H₁₄<CO / CO
NH₂·NH₂
C₆H₅·N:C:O
C₆H₅·N:C:O
C₆H₅·NH·CO·NH·NH₂
C₆H₅·NH·CO·NH·NH₂
α-Phenylcarbamylhydrazone m. p. 211°
β-Phenylcarbamylhydrazone m. p. 161°
NH₂·NH·CO·NH₂
C₆H₅·NH₂
C₆H₅·NH₂
α-Semicarbazone m. p. 236°
β-Semicarbazone m. p. 147°
Heat
H₂SO₄
C₆H₅·NH₂
Heat
Ac₂O
Ac₂O

tural considerations, and since the only justification for a stereochemical explanation is the exclusion of structural differences, we proceed to deal with the possible causes of the foregoing relationships. These are:

1. Dimorphism, condemned by the distinct differences in optical activity which solutions of the respective pairs display under comparable conditions.

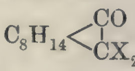
2. Polymerism, which might be suspected from the higher melting point and sparing solubility of the α-compounds. The latter property has precluded application of the freezing-point method of molecular-weight determination except in the case of the α-phenylcarbamylhydrazone; this is normal, and so is the α-semicarbazone in boiling chloroform, whilst for other reasons which become apparent later in this paper it is difficult to believe that the less fusible member of each pair is merely a polymeride of the corresponding β-modification.

3. The structural difference which, depending on the asymmetry of the camphane molecule, renders the types,



$$C_8H_{14}\Big\langle\begin{array}{c}CX_2\\ |\\ CO\end{array}$$

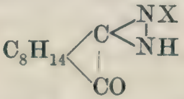
and



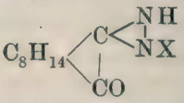
$$C_8H_{14}\Big\langle\begin{array}{c}CO\\ |\\ CX_2\end{array},$$

distinct from one another. The principal objection to this explanation is one which is familiar to all workers with camphor derivatives, namely, the immensely superior reactivity of the α-position. But it is excluded also by the formation of the hydrazones on reducing diazocamphor, supported by the improbability of the above types undergoing interconversion by merely heating the substances at 100—200°.

4. *cis-trans*-Isomerism, also depending on the asymmetry of the camphane nucleus, as represented by the formulæ:



and



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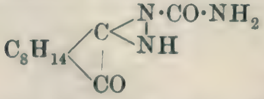
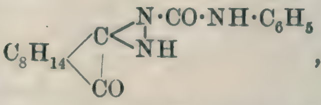
the possibility of which has been indicated by Armstrong and Robertson (Trans., 1905, **87**, 1278). This point would be difficult to argue in the case of the semicarbazones and phenylcarbamylhydrazones if these had the constitution:



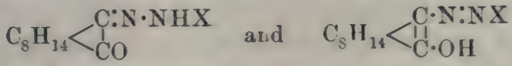
and



,

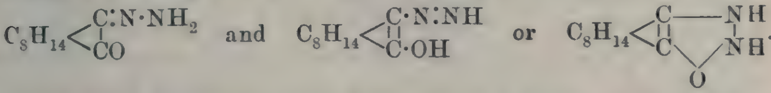
respectively, but is simplified by their experimental relation to the hydrazones, because it is obvious that *cis-trans*-isomerism of the order shown above could not occur in the case of the latter substances.

5. The structural difference arising from enolisation, namely:



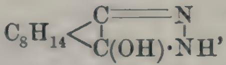
$$C_8H_{14}<\begin{matrix}C{:}N\cdot NHX\\ |\\ CO\end{matrix} \quad\text{and}\quad C_8H_{14}<\begin{matrix}C\cdot N{:}NX\\ \|\\ C\cdot OH\end{matrix}$$

as suggested by Betti in connexion with the phenylhydrazones (*Ber.*, 1899, **32**, 1995). Here again the test is furnished by the simple hydrazones, which would be represented as:



$$C_8H_{14}<\begin{matrix}C{:}N\cdot NH_2\\ |\\ CO\end{matrix} \quad\text{and}\quad C_8H_{14}<\begin{matrix}C\cdot N{:}NH\\ \|\\ C\cdot OH\end{matrix} \quad\text{or}\quad C_8H_{14}<\begin{matrix}C & — & NH\\ \| & & |\\ C & \diagdown O \diagup & NH\end{matrix}.$$

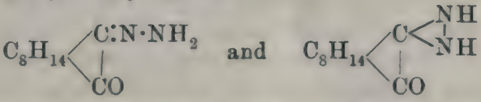
But this enolic formula represents the nitrogen in a condition hopelessly unprotected and quite incompatible with stability, whilst the alternative cycloid could not reasonably be expected to display chemical behaviour practically identical with the azethenoid compound represented by the first of the above expressions. The latter remark applies also to the formula:



$$C_8H_{14}<\begin{matrix}C & = & N\\ | & & |\\ C(OH) & \cdot & NH\end{matrix},$$

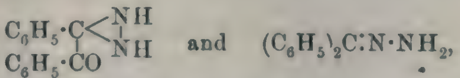
suggested by analogy to Hantzsch's representation of the alkali derivatives from oximinoketones. Thus the keystone of the discussion is the constitution of the simple hydrazones.

6. The structural difference of compounds derived from the azethenoid and cyclic hydrazones:



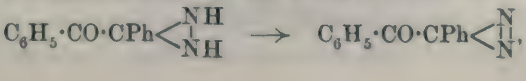
$$C_8H_{14}<\begin{matrix}C{:}N\cdot NH_2\\ |\\ CO\end{matrix} \quad\text{and}\quad C_8H_{14}<\begin{matrix}C<\begin{matrix}NH\\ |\\ NH\end{matrix}\\ |\\ CO\end{matrix}$$

respectively. The discussion of this possibility involves a reference to the early work of Curtius on the interaction of hydrazine hydrate and ketonic substances. In dealing with the constitution of hydrazine derivatives from benzil and benzophenone, Curtius and Thun (*J. pr. Chem.*, 1891, [ii], **44**, 161) and, later, Curtius and Rauterberg (*loc. cit.*, p. 192) distinguish the products by the formulæ:



$$\begin{matrix}C_6H_5\cdot C<\begin{matrix}NH\\ |\\ NH\end{matrix}\\ |\\ C_6H_5\cdot CO\end{matrix} \quad\text{and}\quad (C_6H_5)_2C{:}N\cdot NH_2,$$

respectively. Their principal reasons for doing so were the superior reactivity of the benzophenone derivative towards benzaldehyde, although the benzilhydrazone also condenses with that substance, and the oxidation of the benzilhydrazone to the corresponding derivative of diazomethane by the action of mercuric oxide:



$$C_6H_5\cdot CO\cdot CPh<\begin{matrix}NH\\ |\\ NH\end{matrix} \longrightarrow C_6H_5\cdot CO\cdot CPh<\begin{matrix}N\\ \|\\ N\end{matrix},$$

the benzophenonehydrazone being stated to yield a tetrazone by this treatment:

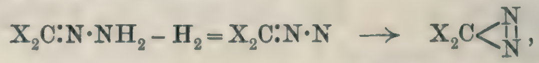
$$(C_6H_5)_2C{:}N{\cdot}NH_2 \longrightarrow (C_6H_5)_2C{:}N{\cdot}N{:}N{\cdot}N{:}C(C_6H_5)_2.$$

The evidence of tetrazone-formation will be found on examination, however, to be noticeably slender, and in the light of our own experiments we suggest that the "tetrazones" derived from benzophenonehydrazone (Curtius and Rauterberg, *loc. cit.*), benzylidenehydrazone (Curtius and Pflug, *loc. cit.*, p. 535), and acetophenonehydrazone (Curtius and Pflug, *loc. cit.*) are unstable derivatives of diazomethane, corresponding with that obtained from benzilhydrazone.

If this suggestion is justified it would, at first sight, appear to confirm the cyclic representation of the hydrazones. But it has been already pointed out that *cis-trans*-isomerism of an unsubstituted cyclic hydrazone does not seem possible, and the direct consequence of revealing isomerism in a simple hydrazone is therefore to discredit the cyclic structure for at least one member of the pair in favour of the azethenoid representation. How, then, is the formation of a diazomethane derivative from an azethenoid hydrazone to be explained? We suggest the following interpretation, first pointing out that it is probably the self-evidence of the conclusion that a hydrazone, convertible into a diazomethane derivative by mercuric oxide, must be derived from a cyclic type, which has obscured the possibility of an alternative explanation. It seems to us most likely that the cause of this change is to be found in the Hofmann-Curtius reaction, which, without quoting other examples (Trans., 1909, **95**, 433; Schroeter, *Ber.*, 1909, **42**, 2336) may be summarised in the equations:

$$X{\cdot}CO{\cdot}NHBr-HBr=X{\cdot}N{:}C{:}O.$$
$$X{\cdot}CO{\cdot}N_3-N_2=X{\cdot}N{:}C{:}O.$$

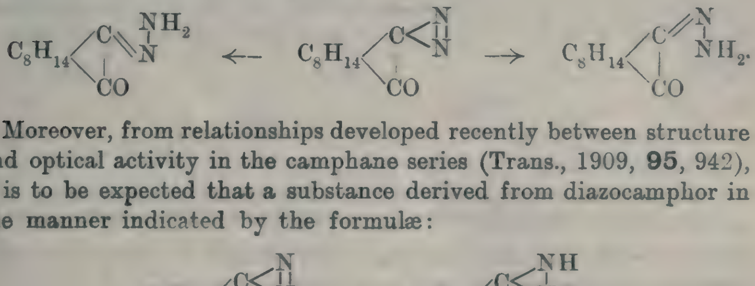
Applying this to the present question, we have to deal with a case of arrested transformation:



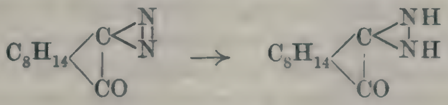
$$X_2C{:}N{\cdot}NH_2-H_2=X_2C{:}N{\cdot}N \longrightarrow X_2C\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right.,$$

it being impracticable for the denuded atom of nitrogen to displace carbon from its position in the molecule, with the result that the azethenoid linking incurs a redistribution of valency.

Although a superficial criticism of this explanation might dismiss it as forced, and less probable than the one at present accepted, it is strongly supported by the following circumstances. As already pointed out, the isomeric camphorquinonehydrazones cannot both have the cyclic structure; if, on the other hand, one were cyclic and the other azethenoid, some difference in behaviour towards an oxidising agent should evince itself. But there is none. The α- and β-hydrazones, dissolved in cold pyridine, have been oxidised with aqueous mercury acetamide to diazocamphor, and the precipitation of mercury takes place instantaneously in both cases. Moreover, by reducing diazocamphor in cold alcohol with ammonium sulphide, both hydrazones have been regenerated. It appears to us that these experiments point incontestably to stereoisomerism of the Hantzsch-Werner type. Theoretical considerations make it clear that at least one of the hydrazones must be azethenoid, and since oxidation of both leads to diazocamphor, the production of a diazomethane derivative from a hydrazone by this step cannot be accepted any longer as evidence of the cyclic structure. Furthermore, the fact that diazocamphor yields both hydrazones on reduction vitiates the conclusion that because diazomethane is cycloid, a hydrogenised diazocamphor must be a cyclic hydrazone. On the other hand, formation of both hydrazones on reducing diazocamphor gives colour to our hypothesis, because if it be admitted that ring-scission occurs on reduction, *anti-* and *syn*-modifications would be produced simultaneously:



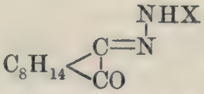
Moreover, from relationships developed recently between structure and optical activity in the camphane series (Trans., 1909, **95**, 942), it is to be expected that a substance derived from diazocamphor in the manner indicated by the formulæ:



would display lower rotatory power than diazocamphor itself, whereas the α- and β-hydrazones of camphorquinone both have distinctly higher molecular rotation. Furthermore, they do not differ greatly from one another in respect of this property, although a considerable difference might be anticipated between an azethenoid and a cyclic hydrazone.

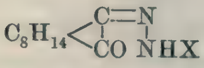
The second chemical distinction which has been mentioned as leading Curtius to differentiate between cyclic and azethenoid hydrazones, namely, condensation with benzaldehyde, corroborates the evidence from oxidation. When suspended in cold water and shaken with this agent, both hydrazones undergo immediate condensation, indicated by a change of colour, since the benzylidene derivative is deep yellow. The final product is the same whether the α- or the β-hydrazone is employed as starting-material, but the deeper colour generated by the latter substance, and the delay in solidification shown by the product, suggest the preliminary formation of an unstable β-benzylidene compound.

Before concluding, we ought to mention that there is one distinction existing between the members of each pair which will doubtless be quoted as evidence in conflict with our explanation. It is a fact that whilst the α-hydrazone, α-semicarbazone, and α-phenylcarbamylhydrazone are colourless, the β-modifications are faintly yellow. It was by a distinction of this order that Armstrong and Robertson (*loc. cit.*) attempted to justify their representation of the phenylmethylhydrazone and phenylbenzylhydrazone of camphorquinone as "phanes," whilst retaining the azethenoid structure for the diphenylhydrazone, and if the same principle were applied to the substances described herein, the colourless α-hydrazone and its derivatives would be represented as cycloid, whilst the yellow β-compounds would be labelled azethenoid. In the foregoing remarks we have endeavoured to show that this cannot be accepted, but even if that evidence could be swept aside, we still hold that the conclusion from colour is in support of our hypothesis, which regards the α- and β-derivatives as *anti-* and *syn-*carbonylic respectively:



$$\mathrm{C_8H_{14}}<\begin{matrix}\mathrm{C{=}N{-}NHX}\\ |\\ \mathrm{CO}\end{matrix}$$

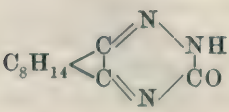
α-Hydrazone, α-semicarbazone, and α-phenylcarbamylhydrazone.



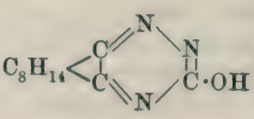
$$\mathrm{C_8H_{14}}<\begin{matrix}\mathrm{C{=}N}\\ |\quad\ |\\ \mathrm{CO\ \ NHX}\end{matrix}$$

β-Hydrazone, β-semicarbazone, and β-phenylcarbamylhydrazone.

For it cannot be denied that from the conflict of views as to the relation between colour and constitution there does emerge this principle, that colour appears to be associated with a concentration of unsaturated atoms. Clearly there is a more intimate massing of such atoms in the β-compounds as represented above than in their isomerides, and it is fair to claim this point as favouring the stereochemical hypothesis. In further support of the latter, it may be stated that the only chemical distinction between the members of each pair which has yet come to light is to be found in the behaviour of the semicarbazones towards aqueous alkali. Whilst the α-semicarbazone forms a yellow solution which does not undergo spontaneous alteration, the dissolved β-semicarbazone quickly loses its colour, and on acidifying the liquid there is liberated the oxytriazine:



or



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production of which is obviously more favoured by the *syn*-carbonylic configuration than by the alternative one.

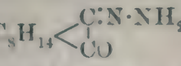
These, then, are our principal reasons for inclining to the stereochemical representation of the camphorquinonehydrazones and their derivatives described in this paper. If this interpretation finds acceptance, it carries with it fresh evidence in support of the Hantzsch-Werner hypothesis.

EXPERIMENTAL.

Action of Hydrazine Hydrate on Camphorquinone.

Azocamphanone.—Twelve grams of hydrazine hydrochloride, dissolved in 100 c.c. of water, were treated with 12 grams of potassium hydroxide, and, when cold, mixed with 33 grams of camphorquinone in 100 c.c. of hot alcohol. During one hour at 40° the appearance of the liquid had completely changed, owing to the separation of a bulky, pale yellow precipitate; this was collected, washed with 50 per cent. alcohol, and found to weigh 29 grams. The product was dissolved in 400 c.c. of boiling alcohol, which deposited lustrous, six-sided, transparent plates, almost rhombohedral in form; becoming deep yellow at 195°, it melted and decomposed at 218°. (Found, $N = 8{\cdot}75$; $C_{20}H_{28}O_2N_2$ requires $N = 8{\cdot}53$ per cent.) This compound is the "azocamphanone" of Angeli (*loc. cit.*), who records 222° as the melting point, whilst Oddo gives 217—218°. It does not reduce hot Fehling's solution, and is not hydrolysed by a hot 20 per cent. solution of alcoholic potassium hydroxide; concentrated hydrochloric acid, however, when mixed with an alcoholic solution and boiled, eliminates hydrazine, but cold concentrated sulphuric acid, although forming a deep yellow solution, does not resolve azocamphanone into hydrazine and camphorquinone. An alcoholic solution does not change when heated with an aqueous solution of mercury acetamide.

When powdered or in separate crystals, azocamphanone appears colourless, but when viewed in bulk it has a yellow tinge, and solutions are deep yellow; 0·3104 gram, dissolved in chloroform and made up to 25 c.c., gave α_D 4°20′ in a 2-dcm. tube, whence $[\alpha]_D$ 174·5° and $[M]_D$ 571°, not 790°, as previously stated in error (Trans., 1909, **95**, 948).

The Isomeric Camphorquinonehydrazones,  $C_8H_{14}<\begin{matrix}C{:}N{\cdot}NH_2\\ |\\ CO\end{matrix}$.—An aqueous solution of hydrazine hydrate prepared from 30 grams of hydrazine sulphate and 24 grams of potassium hydroxide in 150 c.c. of water was mixed with 33 grams of camphorquinone, dissolved in 150 c.c. of hot alcohol. After three hours at 40°, 23 grams of pale brown crystals had separated, quite distinct in appearance from the bulky precipitate of azocamphanone, and a current of steam having been passed through the filtrate until all volatile matter was removed, a further 2 grams crystallised from the hot liquid, so that under these conditions the yield of α-hydrazone amounted to 75 per cent. There was not any azocamphanone or camphorquinone, and after recrystallisation from about 400 c.c. of boiling alcohol, the α-hydrazone separated in long, lustrous, transparent prisms, melting and evolving gas at 206°:

0·2538 gave 0·6189 CO_2 and 0·2037 H_2O. C = 66·51; H = 8·98.
0·1418 „ 18·9 c.c. N_2 at 15° and 751·5 mm. N = 15·43.
$C_{10}H_{16}ON_2$ requires C = 66·66; H = 8·88; N = 15·55 per cent.

The α-hydrazone and its solutions are colourless, but large crystals frequently have a brown tinge; 0·3110 gram, dissolved in chloroform and made up to 25 c.c., gave α_D 7°9′ in a 2-dcm. tube, whence $[\alpha]_D$ 287·4°. The compound is insoluble in petroleum, and is not readily soluble in other media even when these are boiled; acetone or benzene is a convenient solvent from which to obtain it in colourless crystals, but upwards of 100 c.c. of the latter solvent at the boiling point are required to dissolve 1 gram of the substance. It is readily soluble, however, in warm phenol, and sparingly so in cold pyridine.

A solution in chloroform decolorises bromine immediately, and ammoniacal silver oxide is reduced when warmed with the alcoholic solution. On adding solid sodium nitrite to a cold suspension of the α-hydrazone in glacial acetic acid, the salt assumed a transient purple tint, whilst the liquid became yellow and evolved gas; on diluting the acetic acid with water, azocamphanone was precipitated.

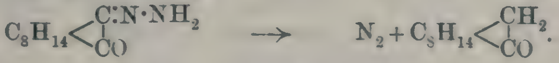
On passing a current of steam through the filtrate from the α-hydrazone as prepared under the foregoing conditions, 3 grams of a straw-yellow, crystalline material were carried over. The yield of this compound, however, was trebled by adding 40 grams of hydrazine hydrate to 50 grams of camphorquinone dissolved in 75 c.c. of alcohol, when the deep yellow colour changed immediately to pale brown; copious precipitation of the α-hydrazone took place after a very short interval, and at the end of half an hour the liquid was filtered and subjected to a current of steam. The solid distillate, consisting of β-hydrazone, weighed 12·5 grams, whilst 2 grams more were obtained by extracting the distilled water (1200 c.c.) with ether; the yield of accompanying α-hydrazone was 66·6 per cent., and if both compounds are required, the above conditions of procedure are the most economical. The β-hydrazone was recrystallised twice from boiling petroleum (b. p. 60—80°), 12 grams requiring 120 c.c. of the solvent, which deposited long, lustrous, straw-yellow needles or transparent prisms, melting at 102°:

0·2038 gave 0·4975 CO_2 and 0·1632 H_2O. C=66·59; H=8·96.
0·1864 „ 26·6 c.c. N_2 at 25° and 754 mm. N=15·79.
$C_{10}H_{16}ON_2$ requires C=66·66; H=8·88; N=15·55 per cent.

The substance has a faint odour suggesting that of bornylamine; it is readily soluble in organic media, excepting petroleum. A solution containing 0·3134 gram, made up to 25 c.c. with chloroform, gave α_D 5°48′ in a 2-dcm. tube, whence $[\alpha]_D$ 231·3°. An alcoholic solution reduces cold ammoniacal silver oxide, and a solution in chloroform decolorises bromine immediately.

Interconversion of the Hydrazones.

On melting the β-hydrazone, it was noticed that if the temperature of the bath is raised to 150—160° the liquid solidifies, and this change was found to be due to conversion into the isomeride, which is readily isolated by recrystallisation from hot alcohol. The converse transformation cannot be brought about by merely melting the α-hydrazone, because this modification slowly loses nitrogen at 205—210°, yielding camphor:



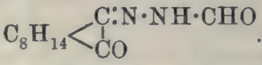
$$C_8H_{14}<\begin{matrix}C{:}N\cdot NH_2\\ |\\ CO\end{matrix} \longrightarrow N_2 + C_8H_{14}<\begin{matrix}CH_2\\ |\\ CO\end{matrix}.$$

If, however, the α-hydrazone is dissolved in molten paraffin wax, and maintained at 180° during a few minutes, it is a simple matter to demonstrate the formation of the β-hydrazone by suspending the product in hot water, and passing a current of steam through the liquid, when the volatile modification is carried into the condenser.

Action of Sulphuric Acid on the Hydrazones.

The hydrazones behave exactly alike towards sulphuric acid. When covered with the warm agent of 30 per cent. strength, a clear solution is formed almost immediately, and this at once becomes turbid, setting to a paste of azocamphanone in the course of a few minutes; on extracting the filtered product with boiling alcohol, crystals of hydrazine sulphate remain undissolved. With 10 per cent. acid, a clear solution is not produced, because the dissolution of the hydrazone is overtaken by the separation of azocamphanone.

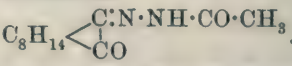
Acyl Derivatives of the Hydrazones.

The α-Formyl Derivative,  $C_8H_{14}<\substack{C:N\cdot NH\cdot CHO \\ | \\ CO}$.—On dissolving 1 gram of the α-hydrazone in 10 grams of formic acid (D 1·2), the pale yellow solution remained clear during a few seconds, when a shower of crystals separated; the derivative was recrystallised from boiling alcohol, of which about 70 c.c. were required by 1 gram, and was deposited in colourless, lustrous, six-sided plates, which displayed frequent twinning. It melts at 234°:

0·1240 gave 14·6 c.c. N_2 at 18° and 757 mm. N = 13·54.
$C_{11}H_{16}O_2N_2$ requires N = 13·45 per cent.

The formyl derivative is insoluble in boiling petroleum, and dissolves sparingly in methyl alcohol, benzene, acetone, and chloroform unless these solvents are heated, 15 c.c. of the last-named, for example, dissolving about one decigram until warmed; it is more readily soluble in pyridine and glacial acetic acid. A solution containing 0·1720 gram, made up to 25 c.c. with chloroform, gave α_D 3°33′ in a 2-dcm. tube, whence $[\alpha]_D$ 258·0°. On adding ferric chloride to an alcoholic solution, a pale brown coloration is developed, whilst that with copper acetate is grass-green. Aqueous alkalis dissolve the substance readily, producing a bright yellow solution, and on adding ferrous sulphate to the diluted liquid a dark bluish-green precipitate is formed; when the alkaline solution is left at the laboratory temperature, the colour quickly fades, and the α-hydrazone separates.

The same formyl derivative was also produced by the action of the acid on the β-hydrazone. An attempt to prepare a benzoyl derivative by the action of benzoyl chloride on the formyl compound dissolved in pyridine was not successful.

The α-Acetyl Derivative,  $C_8H_{14}<\substack{C:N\cdot NH\cdot CO\cdot CH_3 \\ | \\ CO}$.—Although dissolving readily in cold formic acid, the α-hydrazone is only moderately soluble in cold glacial acetic acid; it dissolves on warming the liquid, but does not crystallise readily even on dilution, owing to partial acetylation. The substance was therefore warmed with five parts of acetic anhydride, when the acetyl derivative separated as a paste of crystals at the moment of complete dissolution in the hot liquid; recrystallisation from a considerable proportion of boiling alcohol gave long, lustrous, snow-white needles, melting and decomposing at 239°:

0·1047 gave 11·8 c.c. N_2 at 17° and 760 mm. N = 13·07.
$C_{12}H_{18}O_2N_2$ requires N = 12·61 per cent.

A solution containing 0·2226 gram, made up to 20 c.c. with chloroform, gave α_D 5°54′ in a 2-dcm. tube, whence $[\alpha]_D$ 265·5°. The compound dissolves freely in dilute aqueous alkali, developing a bright yellow coloration, and the solution yields an intense bluish-green precipitate with ferrous sulphate; 0·2083 gram, dissolved in 5 c.c. of 10 per cent. sodium hydroxide and diluted to 25 c.c. with water, gave α_D 4°12′ in a 2-dcm. tube, whence $[\alpha]_D$ 252·0°. In process of time, the colour of the alkaline solution fades, and the α-hydrazone separates from the liquid.

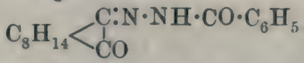
The β-Acetyl Derivative.—On dissolving the β-hydrazone in five parts of cold acetic anhydride, the temperature rose slightly, and long, flat, transparent prisms began to separate in the course of a few minutes; after recrystallisation from boiling petroleum, the substance was found to be pale yellow, and melted at 150°:

0·1297 gave 14·5 c.c. N_2 at 18° and 760 mm. N = 12·91.

$C_{12}H_{18}O_2N_2$ requires N = 12·61 per cent.

A solution containing 0·3890 gram, made up to 25 c.c. with chloroform, gave α_D 6°58′ in a 2-dcm. tube, whence $[\alpha]_D$ 223·8°. The solution in aqueous alkali has the same appearance as that of the α-acetyl derivative, developing a similar precipitate with ferrous sulphate; in the course of some hours, the yellow colour fades, and the liquid deposits crystals of the α-hydrazone.

When the β-acetyl derivative is heated at temperatures above its melting point, varying proportions of the α-acetyl compound are produced, but the conversion is not complete; moreover, on heating the α-acetylhydrazone in acetic anhydride, a certain amount of the β-isomeride may be isolated from the product.

The α-Benzoyl Derivative,  $C_8H_{14}\left\langle\begin{matrix}C{:}N\cdot NH\cdot CO\cdot C_6H_5\\ |\\ CO\end{matrix}\right.$.—The α-hydrazone requires about 25 parts of pyridine to maintain a clear solution at zero, and on adding the calculated amount of benzoyl chloride, also dissolved in ice-cold pyridine, the hydrochloride of the base separated, the benzoyl derivative being precipitated on dilution with water; recrystallisation from boiling alcohol, in which it is sparingly soluble, gave tough, lustrous, snow-white needles, becoming yellow above 200°, and melting at 219—222°, according to the rate at which the temperature is raised:

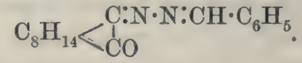
0·1322 gave 11·4 c.c. N_2 at 16° and 757 mm. N = 10·01.

$C_{17}H_{20}O_2N_2$ requires N = 9·86 per cent.

The substance is not readily soluble in chloroform, and a solution containing 0·2135 gram, made up to 50 c.c. with this solvent, gave α_D 1°45′ in a 2-dcm. tube, whence $[\alpha]_D$ 204·9°. Although in part dissolved by 2 per cent. aqueous sodium hydroxide, the benzoyl derivative did not form a clear solution; 0·1904 gram, suspended in about 20 c.c. of the agent, was made up to 50 c.c. with absolute alcohol, the clear, deep yellow liquid giving α_D 1°50′ in a 2-dcm. tube, whence $[\alpha]_D$ 240·7°.

On attempting to prepare a benzoyl derivative of the β-hydrazone, the principal product was found to consist of the substance just described, but the residue from the mother liquor remained oily during many months, suggesting that both isomerides are formed. The α-benzoyl derivative was obtained also by mixing equal quantities of camphorquinone and benzoylhydrazine in dilute alcohol, crystals separating after two hours at 40°; in this case, also, the filtrate deposited an oil, indicating the presence of a mixture.

Benzylidene Derivative of Camphorquinonehydrazone,



$$C_8H_{14}<\begin{matrix}C{:}N\cdot N{:}CH\cdot C_6H_5\\ | \\ CO\end{matrix}.$$

The α-hydrazone was finely powdered, mixed with the calculated amount of benzaldehyde, and heated with a few c.c. of alcohol during two or three minutes; crystals did not separate on cooling, but water precipitated a yellow oil, which quickly became solid, and was recrystallised from boiling petroleum (b. p. 60—80°). The massive, yellow crystals melted at 109·5°:

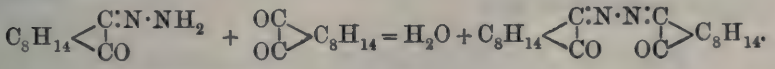
0·1253 gave 12·0 c.c. N_2 at 20·5° and 758 mm. N = 10·90.

$C_{17}H_{20}ON_2$ requires N = 10·44 per cent.

The substance is freely soluble in chloroform, benzene, acetone, alcohol, and ethyl acetate, but only moderately so in warm petroleum; a solution containing 0·3035 gram, made up to 20 c.c. with chloroform, gave α_D 4°50′ in a 2-dcm. tube, whence $[\alpha]_D$ 159·2°. It is also produced immediately on shaking the finely powdered hydrazone with water and benzaldehyde, but the method is not convenient, as a portion of the hydrazone remains mechanically protected.

The same benzylidene derivative is produced on agitating the β-hydrazone suspended in water with the aldehyde, the deep yellow colour of the condensation product becoming noticeable immediately. Owing to the solubility of the β-hydrazone in water, none escapes combination, but the product remains liquid during many days, although rapidly becoming solid when heated to 100° and scratched.

Another example of the capacity of the hydrazones for taking part in condensation changes was given by heating an alcoholic solution of the α-hydrazone and camphorquinone in molecular proportion during twelve hours under reflux, when azocamphanone was produced:



$$C_8H_{14}\left<\begin{matrix}C{:}N\cdot NH_2\\ \vert\\ CO\end{matrix}\right. + \left.\begin{matrix}OC\\ \vert\\ OC\end{matrix}\right>C_8H_{14} = H_2O + C_8H_{14}\left<\begin{matrix}C{:}N\cdot N{:}C\\ \vert \qquad\quad \vert\\ CO \qquad OC\end{matrix}\right>C_8H_{14}.$$

Oxidation of the Hydrazones to Diazocamphor.

Since it was desirable to study the oxidation of the hydrazones under conditions precluding the likelihood of preliminary interconversion, it occurred to us that mercury acetamide, owing to its solubility in cold water, might be a more suitable agent than mercuric oxide, a study of the acetamide compound having shown that it acts rapidly on primary hydrazines with precipitation of mercury (Trans., 1898, **73**, 783). Experiment showed that the behaviour of the isomeric hydrazones of camphorquinone towards this agent distinguishes itself sharply from the indifference of azocamphanone. It having been first ascertained that the β-hydrazone is not transformed into the isomeride by dissolution in pyridine, 1 gram dissolved in 3 c.c. of the cold solvent was treated with 2 grams of mercury acetamide in 3 c.c. of cold water, the metal being precipitated immediately. The production of the diazo-compound was indicated on extracting with ether, which became deep yellow, and, after evaporation, the pyridine residue yielded 0·8 gram of diazocamphor on dilution with water; recrystallisation from petroleum (b. p. 40°) gave long, striated, yellow prisms, melting at 73—74°.

Procedure in the case of the α-hydrazone was modified by the sparing solubility of the substance, 5 grams of which were dissolved in 80 c.c. of hot pyridine, cooled to 50—60°, and treated with 10 grams of mercury acetamide in 30 c.c. of warm water; mercury was precipitated immediately, and 4 grams of diazocamphor obtained. A solution containing 0·4605 gram of the diazo-compound, made up to 25 c.c. with chloroform, gave α_D 4°58′ in a 2-dcm. tube, whence $[\alpha]_D$ 134·8°.

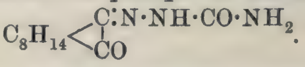
Reduction of Diazocamphor to the Hydrazones.

A 20 per cent. solution of diazocamphor in absolute alcohol was saturated with hydrogen sulphide without undergoing any change in appearance, but on adding a few drops of dilute ammonia and again passing the gas, the liquid became pale brown, and gradual separation of the α-hydrazone took place; on subjecting the filtrate to steam distillation, a small proportion of the β-hydrazone was carried over. As it is a matter of importance to establish the production of both compounds without question, the experiment was repeated at zero, when it was found that the precipitation of the α-hydrazone was diminished, and the yield of β-hydrazone was proportionately increased.

Reduction of the α-Hydrazone to α-Aminocamphor.

Owing to the readiness with which the hydrazones undergo acetylation, a certain amount of the α-acetyl derivative is formed on attempting to reduce the α-hydrazone with zinc dust and acetic acid; it is precipitated, however, when the acid is neutralised. On adding a further quantity of alkali to the filtrate, ammonia is set free, and ether extracts aminocamphor, which may be identified by conversion into the oxime; a specimen of aminocamphoroxime obtained in this way melted at 144—145°.

The Isomeric Camphorquinonesemicarbazones,



$$C_8H_{14}<\begin{matrix}C\colon N\cdot NH\cdot CO\cdot NH_2\\ |\\ CO\end{matrix}.$$

The discovery of a second camphorquinonesemicarbazone arose from the observation that on evaporating the filtrate from the substance described by Lapworth and Chapman, there is deposited an oil which, by treatment with very dilute aqueous alkali, is divisible into two solids; one passes into solution, and consists of the derivative already known, whilst the new semicarbazone remains suspended.

A solution containing 33·2 grams of camphorquinone in 150 c.c. of alcohol was mixed with semicarbazide acetate prepared from 22·2 grams of the hydrochloride and 27 grams of crystallised sodium acetate in 100 c.c. of water; the liquid, from which crystals of the α-semicarbazone quickly separated, was transferred to a stoppered filtering flask connected with a water-pump, the alcohol being evaporated at the laboratory temperature during six to eight hours, when drops of oil became noticeable among the crystals. From the resulting sludge about 16 grams of the less soluble α-semicarbazone were filtered, the mother liquor being poured into water and treated with alkali hydroxide until a faint yellow colour persisted; the suspended oil became solid when stirred, and consisted of the more soluble β-semicarbazone mixed with a small proportion of the isomeride. In order to remove the latter, the filtered product was ground three or four times with 10 c.c. of 2 per cent. aqueous sodium hydroxide, the filtration necessary after each extraction being carried out as quickly as possible, because although the α-semicarbazone dissolves in weak alkali without delay, the β-modification is also soluble, but very slowly. The pale yellow powder was then extracted twice with 300 c.c. of boiling water, the crystalline deposit (6 grams) from this being recrystallised from 25 c.c. of warm benzene, to which the same volume of petroleum was added. At this stage the purification was complicated by the fact that following closely on the slender, yellow crystals of the β-semicarbazone there appeared opaque nodules containing the isomeride.

Camphorquinone-α-semicarbazone is the substance described by Lapworth and Chapman (*loc. cit.*). It crystallises from alcohol in lustrous, colourless prisms, melting and evolving gas at 236°, after sintering and becoming yellow at about 230°; it is much less readily soluble in organic media than the isomeride, and is insoluble in petroleum. A solution containing 0·3152 gram, made up to 20 c.c. with methyl alcohol, gave α_D 8°45′ in a 2-dcm. tube, whence $[\alpha]_D$ 277·6°. As distinguished from the β-compound, it dissolves immediately in dilute alkali, and 0·3344 gram in sufficient potassium hydroxide, made up to 25 c.c. with water, gave α_D 8°55′ in a 2-dcm. tube, whence $[\alpha]_D$ 333·3°; this remained constant during six days, and the semicarbazone precipitated from the solution by acetic acid was unchanged material. Nevertheless, on heating with 10 per cent. potassium hydroxide during three to four days, camphor was gradually produced. Cold concentrated sulphuric acid dissolves the α-semicarbazone, and gradually changes it to azocamphanone, which is precipitated on pouring the liquid into water; if, however, the hot acid is used, a certain amount of camphorquinone is produced. An estimation of the molecular weight in boiling chloroform gave 236 instead of 223.

Camphorquinone-β-semicarbazone crystallises in pale yellow prisms, melts at 147°, and is readily soluble in alcohol, acetone, ethyl acetate, chloroform, ether, or benzene, but dissolves only sparingly in hot water or boiling petroleum:

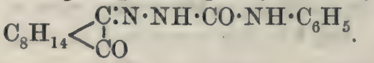
0·2328 gave 0·5037 CO_2 and 0·1539 H_2O. C = 59·03; H = 7·66.
0·3225 „ 54·8 c.c. N_2 at 25° and 754 mm. N = 18·79.
$C_{11}H_{17}O_2N_3$ requires C = 59·19; H = 7·62; N = 18·83 per cent.

A solution containing 0·3152 gram, made up to 20 c.c. with methyl alcohol, gave α_D 6°20′ in a 2-dcm. tube, whence $[\alpha]_D$ 200·9°. When covered with aqueous alkali hydroxide, the β-semicarbazone does not appear to dissolve; if, however, the solid substance is thrown into hot 10 per cent. sodium hydroxide, there is produced immediately a deep yellow solution, the colour of which gradually fades, owing to the formation of the oxytriazine (see below). On raising the temperature of the fused β-semicarbazone to about 190°, the substance became solid, and the α-semicarbazone was found to have been produced.

Conversion of the Semicarbazones into the Acetylhydrazones.

The semicarbazones were separately heated with boiling acetic anhydride during one hour, the solid product obtained in each case, on pouring the liquid into water, being found to consist of a mixture of the α- and β-acetyl derivatives of the hydrazones. The transformation was not easy to establish experimentally, because the relative solubility of the acetyl derivatives in alkali exactly resembles that of the semicarbazones themselves, and as the melting points of the latter differ from those of the respective acetyl hydrazones by 3° only in each case, the preliminary experiments led to the supposition that the semicarbazones are directly interconvertible by the action of the agent in question.

The Isomeric Camphorquinonephenylcarbamylhydrazones,



$$C_8H_{14}<\begin{matrix}C{:}N\cdot NH\cdot CO\cdot NH\cdot C_6H_5\\ |\\ CO\end{matrix}.$$

These derivatives were prepared by three different methods.

(1) Action of hot aniline on the α- and β-semicarbazones, each of which gave both phenylcarbamylhydrazones.

(2) Condensation of camphorquinone with phenylcarbamylhydrazide, also yielding a mixture.

(3) Interaction of phenylcarbimide and the α- and β-hydrazones, which led to the individual phenylcarbamylhydrazones, respectively.

Camphorquinone-α-phenylcarbamylhydrazone.—Four grams of the α-semicarbazone were dissolved in 20 c.c. of aniline, and heated ten minutes at the boiling point of the solvent, ammonia being liberated freely before this temperature was reached; the cooled liquid was diluted with its volume of alcohol, and poured into 200 c.c. of 10 per cent. acetic acid at zero. The precipitated oil quickly hardened when scratched, and on dissolving the product in 80 c.c. of hot methyl alcohol, the α-phenylcarbamylhydrazone crystallised in thick, colourless plates, melting at 211°, whilst the isomeride remained dissolved:

0·2494 gave 0·6096 CO_2 and 0·1656 H_2O. C = 66·67; H = 7·43.

0·1660 „ 20·3 c.c. N_2 at 24° and 761·5 mm. N = 13·75.

$C_{17}H_{21}O_2N_3,\frac{1}{2}CH_4O$ requires C = 66·64; H = 7·30; N = 13·33 per cent.

The transparent crystals became opaque in the steam-oven, owing to loss of crystal-alcohol:

0·2462 gave 0·6158 CO_2 and 0·1546 H_2O. C = 68·23; H = 7·03.

$C_{17}H_{21}O_2N_3$ requires C = 68·23; H = 7·03 per cent.

Ordinary solvents, excepting petroleum, dissolve the substance readily, but, unlike the α-semicarbazone, it is insoluble in cold aqueous alkali hydroxide, although dissolving when heated, with development of a yellow coloration. A solution containing 0·2207 gram, made up to 25 c.c. with chloroform, gave α_D 4°3′ in a 2-dcm. tube, whence $[\alpha]_D$ 229·3°. An estimation of the molecular weight by depression of the melting point of benzene gave 327 instead of 299.

Camphorquinone-β-phenylcarbamylhydrazone.—From the mother liquor of the foregoing substance there gradually separated long, slender, silky needles, in which a few small crystals of the α-compound were embedded, and as the latter remained undissolved on rapidly warming the liquid, it was possible to isolate the β-modification without much difficulty, the final recrystallisation being effected by adding petroleum to a solution of the needles in benzene. The substance is very pale yellow, and melts at 161°:

0·2142 gave 0·5346 CO_2 and 0·1372 H_2O. C = 68·10; H = 7·17.
0·1062 „ 13·9 c.c. N_2 at 24° and 754 mm. N = 14·55.
$C_{17}H_{21}O_2N_3$ requires C = 68·23; H = 7·03; N = 14·09 per cent.

In all common media the solubility of the β-phenylcarbamylhydrazone scarcely differs from that of the isomeride, but the tendency to form supersaturated solutions is much greater. A solution containing 0·2128 gram, made up to 25 c.c. with chloroform, gave α_D 3°16′ in the 2-dcm. tube, whence $[\alpha]_D$ 191·9°.

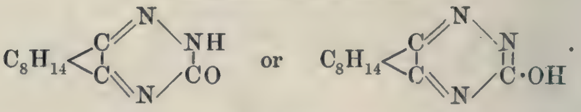
As in the case of the β-semicarbazone, transformation into the α-modification was readily accomplished by heating the β-phenylcarbamylhydrazone above its melting point; the clear liquid which had been carried to 200° remained vitreous on cooling, but immediately became crystalline on being scratched in presence of a small quantity of methyl alcohol.

In preparing the phenylcarbamylhydrazones by the foregoing method, it was noticed that the proportion of the two modifications depends on the duration of heating and on the temperature reached. This is explained by the fact that either is convertible into the other isomeride by the action of hot aniline, each individual yielding an equilibrium mixture when a solution in that base is heated until the solvent boils; roughly speaking, the relation between the constituents of this mixture is $\alpha : \beta = 2 : 1$.

The second process for obtaining the phenylcarbamylhydrazones was practised by mixing solutions containing 5 grams of camphorquinone and 4·5 grams of phenylcarbamylhydrazide, $C_6H_5\cdot NH\cdot CO\cdot NH\cdot NH_2$, each in 15 c.c. of hot methyl alcohol, and heating the liquid on the water-bath during a few minutes; 2·8 grams of the α-phenylcarbamylhydrazone separated on cooling, whilst the mother liquor deposited a mixture of this with the characteristic, silky needles of the β-modification.

The third method is the most convenient when the hydrazones are available, because it leads to the individuals, and thus obviates the necessity of a tedious separation. The finely powdered α-hydrazone (1·8 gram), suspended in 250 c.c. of boiling benzene, in which it was not completely soluble, was heated with 3 grams of phenylcarbimide on the water-bath during two hours, when the liquid did not deposit crystals on cooling. After distilling off the solvent until only 30 c.c. remained, twice this volume of petroleum was added, precipitating 2·7 grams of a crystalline powder, readily identified with the α-phenylcarbamylhydrazone on recrystallisation. In preparing the β-modification by this process, 0·9 gram of the β-hydrazone, dissolved in 10 c.c. of benzene, was treated with 0·7 gram of phenylcarbimide, the mixture being left at the laboratory temperature, and after the lapse of twelve hours diluted with petroleum until pale yellow needles appeared; after recrystallisation it melted at 161°, and did not depress the melting point of the β-phenylcarbamylhydrazone prepared by the other methods.

Camphane-oxytriazine,



Whilst the α-semicarbazone is dissolved immediately by aqueous alkali hydroxide, forming a permanent yellow solution, the β-modification is transformed into the anhydride represented above, the conversion taking place at rates depending on the temperature.

Camphorquinone-β-semicarbazone was covered with 10 parts of 10 per cent. aqueous sodium hydroxide, and shaken at intervals during five hours, when the solid substance, at first coloured yellow by the agent, had passed into a colourless solution. After extraction with ether, dilute sulphuric acid was added until the initial precipitate was redissolved, when the liquid was shaken eight times with ether; the solvent deposited 85 per cent. of viscous residue, which quickly solidified. Recrystallisation from warm benzene, to which petroleum was added, gave colourless, transparent pyramids, melting at 166—167°:

0·2183 gave 0·5137 CO_2 and 0·1406 H_2O. C = 64·18; H = 7·21.
0·1950 „ 35·6 c.c. N_2 at 21° and 759 mm. N = 20·75.
$C_{11}H_{15}ON_3$ requires C = 64·39; H = 7·31; N = 20·49 per cent.

The substance is somewhat readily soluble in warm water, and does not crystallise completely on cooling; alcohol, ether, chloroform and benzene dissolve it readily, but it is insoluble in petroleum. It does not reduce Fehling's solution, and when heated with ammoniacal silver oxide yields a voluminous, white precipitate, freely soluble in ammonia. A solution in sodium carbonate is strongly alkaline, and gives a transient violet precipitate with ferrous sulphate, becoming bright green when excess is added; copper salts produce an apple-green precipitate, also formed by nickel sulphate, excess of which yields a clear solution. The optical activity of the oxytriazine and its derivatives is very much lower than that of the foregoing compounds of camphorquinone; a solution containing 0·2855 gram, made up to 25 c.c. with chloroform, gave α_D 0°31′ in a 2-dcm. tube, whence $[\alpha]_D$ 22·6°.

The *acetyl* derivative was readily formed on heating the oxytriazine with acetic anhydride; after recrystallisation from a mixture of benzene and petroleum, it melted at 168—169°:

0·1765 gave 0·4096 CO_2 and 0·1127 H_2O. C = 63·30; H = 7·14.
$C_{13}H_{17}O_2N_3$ requires C = 63·16; H = 6·88 per cent.

The substance dissolves freely in cold benzene, chloroform, acetone, or methyl alcohol, but is less readily soluble in ethyl alcohol or ethyl acetate, from which it crystallises in lustrous, colourless needles. A solution containing 0·2444 gram, made up to 20 c.c. with chloroform, gave α_D 1°2′ in a 2-dcm. tube, whence $[\alpha]_D$ 42·2°.

The *benzoyl* derivative, prepared by the action of benzoyl chloride in pyridine solution and purified by precipitation from acetic acid, followed by recrystallisation from a mixture of benzene and petroleum, melted at 193—194°:

0·2021 gave 0·5150 CO_2 and 0·1108 H_2O. C = 69·51; H = 6·13.
$C_{18}H_{19}O_2N_3$ requires C = 69·90; H = 6·15 per cent.

The compound is freely soluble in cold acetone or chloroform, but ethyl acetate, methyl alcohol, benzene, or ethyl alcohol dissolve it less readily, and it is very sparingly soluble in boiling petroleum. A solution containing 0·2808 gram, made up to 20 c.c. with chloroform, gave only α_D 0°13′ in a 2-dcm. tube, whence $[\alpha]_D$ 7·7°.

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CCXXVI.—*The Effect of Temperature on the Equilibrium* $2CO \rightleftharpoons CO_2 + C$.

By THOMAS FRED ERIC RHEAD and RICHARD VERNON WHEELER.

THE fact that carbon monoxide dissociates under the influence of heat, yielding carbon dioxide and carbon, or, in other words, the fact that the reaction:

$$CO_2 + C = 2CO$$

is reversible, was discovered by H. Sainte-Claire Deville in 1864 (*Compt. rend.*, 1864, **59**, 873; 1865, **60**, 317) by means of his "hot-cold" tube. He was able to observe only a small degree of dissociation at a temperature a little lower than the melting point of silver, whilst at temperatures above 1000° none at all could be detected.

Since it was assumed that the degree of dissociation of carbon monoxide, like that of carbon dioxide and steam, should increase with increased temperature, doubt was cast on Deville's first experiments, and it was suggested that the formation of carbon dioxide and the deposition of carbon were due to the chemical action of the glaze of the porcelain tubes he employed.

In 1869 Sir Lothian Bell (*Journ. Chem. Soc.*, **22**, 203), while studying the reactions taking place in the blast-furnace, found that such portions of the iron ore as had been subjected to the action of carbon monoxide at comparatively low temperatures in the upper part of the furnace were impregnated with carbon, presumably arising from the dissociation of the gas. He thereupon instituted laboratory experiments to determine the action of carbon monoxide on different oxides at different temperatures.

As a result of these experiments, Bell was able to state that the reduced metal was as effective as the oxide in determining the decomposition of carbon monoxide, and he gave the equation of the reaction as being:

$$2CO = CO_2 + C.$$

He also showed that the oxides of nickel and cobalt and the reduced metals acted in a similar manner to iron oxide and reduced iron.

The influence of temperature on the amount of decomposition in a given time was also studied by Bell, comparative figures being obtained from the quantities of carbon deposited. This is well shown in the following series of experiments, in which carbon monoxide was passed slowly over reduced iron at different temperatures during six hours:

Temperature	250°	400°	500°	600°	800°
Carbon deposited. Grams per 100 grams of iron	4·7	181	95	6	0·3

It is thus apparent that a low temperature favours the decomposition, a result which explains the failure of Deville and others to obtain evidence of dissociation at 1000°, and is in accordance with the fact that the reaction $2CO = CO_2 + C$ is exothermic. The heat of reaction is shown by the following equations:

$$\begin{array}{lll} & (1). & CO + O = CO_2 + 68{\cdot}0 \text{ Kg.C. units.} \\ & (2). & C \;\; + O = CO \;\, + 29{\cdot}0 \quad ,, \quad ,, \\ \text{whence} & & 2CO = CO_2 + C + 39{\cdot}0 \quad ,, \quad ,, \end{array}$$

Since the reaction is reversible, an equilibrium must be established between the quantities of carbon dioxide and monoxide that can exist together in the presence of carbon; and, in accordance with van't Hoff's principle of mobile equilibrium, the quantity of carbon monoxide will be increased by lowering the temperature.

The equilibrium at different temperatures has been studied by O. Boudouard (*Ann. Chim. Phys.*, 1901, [vii], **24**, 5), who has given figures for 650°, 800°, and 925°.

In studying the reaction $2CO \rightarrow CO_2 + C$, Boudouard made use of iron, nickel, and cobalt as catalysts. The finely divided metals were obtained by impregnating broken pumice with the nitrates and igniting, the oxides thus formed being afterwards heated in a stream of carbon monoxide until reduction was considered to be complete.

For the experiments at temperatures below 700°, glass tubes, 6 to 7 cm. long and 1·5 cm. in diameter, were used, the total volume of gas being from 12 to 15 c.c. Above 700°, a porcelain tube, 40 cm. long and of 2·4 cm. internal diameter, was employed, the pumice containing the catalyst occupying the middle 10 cm. of the tube, and the remainder being packed with broken porcelain.

The main results were as follow:

Temperature.	Catalyst.	Duration of heating.	Carbon dioxide, per cent.
445°	iron	6 hours	100
445	nickel	1 hour	100
445	cobalt	1 ,,	100
650	cobalt	7 ,,	61
800	nickel	4 ,,	6·7
800	cobalt	4 ,,	6·5

In one experiment at 445°, using a very small quantity of iron oxide (reduced by carbon monoxide) as catalyst, Boudouard obtained 52·3 per cent. of carbon dioxide and 47·7 per cent. of carbon monoxide remaining after six hours' heating.

The reverse reaction, $CO_2 + C \longrightarrow 2CO$, was studied in a similar manner, but without the use of catalysts, purified wood charcoal being employed. The carbon was heated in an atmosphere of carbon dioxide in tubes sealed at one end, with the other end open and bent so as to dip under mercury, the object being to avoid bursting of the tubes due to increased pressure as the reaction proceeded.

The results were as follow:

Temperature.	Duration of heating, hours.	Carbon dioxide, per cent.
650°	9	62·4
650	12	61·5
800	6	6·7
800	6	6·3

In addition to the above, two experiments were made at 925°, in which a measured volume of carbon dioxide was passed in a slow stream through the heated charcoal, and the resulting gases bubbled through baryta water, the barium carbonate that was precipitated being afterwards weighed. Assuming that a single passage of the carbon dioxide over the heated charcoal was sufficient to establish equilibrium, Boudouard calculated from one experiment 3·3 per cent., and from the other 4·5 per cent., of carbon dioxide remaining in equilibrium with carbon monoxide over carbon at 925°.

Boudouard's experiments prove that the equilibrium ratio CO/CO_2 in contact with carbon is a function of temperature, and the results are in general agreement with the laws respecting equilibria in gaseous systems.

R. Schenck and F. Zimmermann (*Ber.*, 1903, **36**, 1), while studying more particularly the order of the reactions taking place, have been able to prove that the oxides of iron, nickel, and cobalt are quite ineffective in determining the dissociation of carbon monoxide, and that it is only the reduced metals that act catalytically. This is in direct opposition to the views advanced by Boudouard. At the same time Schenck and Zimmermann give results for the equilibrium at low temperatures (445° and 508°) that are entirely at variance with those of Boudouard. At 445° Boudouard regards the dissociation of carbon monoxide as complete; while Schenck and Zimmermann, using reduced iron as catalyst, obtained 52·8 per cent. of carbon monoxide as the quantity remaining in equilibrium at that temperature. It is interesting to note that this figure agrees fairly well with that obtained by Boudouard when using only a small quantity of iron as catalyst (a result which he discards), and it seems probable that in those experiments, otherwise inexplicable, in which he obtained complete decomposition of carbon monoxide, the oxides of the metals used as catalysts were incompletely reduced before the tubes were sealed, and that oxidation of the carbon monoxide took place.

We considered it desirable to determine the equilibrium ratio more accurately and for a greater number of temperatures, avoiding the use of catalysts, for Boudouard's method of experiment did not appear to us to be calculated to give very accurate results, and his figures were not in agreement with those obtained by us during the course of an investigation on the mode of burning of carbon on which we are still engaged.

The method we have adopted has been to circulate carbon dioxide continuously over purified wood charcoal packed in a porcelain tube, and heated in an electric resistance furnace.

We have obtained in this manner the following figures for the percentages of carbon dioxide and monoxide that are in equilibrium in the presence of excess of carbon at different temperatures:

Temperature.	Carbon dioxide.	Carbon monoxide.
	Per cent. by volume.	
850°	6·23	93·77
900	2·22	97·78
950	1·32	98·68
1000	0·59	99·41
1050	0·37	99·63
1100	0·15	99·85
1200	0·06	99·94

The percentages are calculated as those of the nitrogen-free gases. The gases usually contained from 1 to 2 per cent. of nitrogen.

In Le Chatelier's general formula for equilibrium in gaseous systems:

$$500\int L\frac{dT}{T} + (N' - N)\log_e P + \log_e \frac{c_1^{n_1}.c'^{n'_1}_1\ldots}{c_2^{n_2}\,c'^{n'_2}_2\ldots} = k$$

L = the total heat of the reaction at absolute temperature T.

P = the pressure in atmospheres.

N and N' = the number of molecules on the left- and on the right-hand side of the equation.

n_1, n'_1,... and n_2, n'_2,... = the number of molecules of the different substances taking part in the reaction, index 1 meaning the initial and index 2 the final system.

c_1, c'_1,... and c_2, c'_2,... = the concentrations of the different substances, indices as above.

In the system:

$$2CO \rightleftarrows CO_2 + C$$

$n_1 = 2$; $n_2 = 1$; $n'_2 = 0$; $c'_2 = 0$.

If the system is in equilibrium at atmospheric pressure, $P = 1$, and the expression

$$(N' - N)\log_e P = 0.$$

Assuming with Le Chatelier that the heat of reaction is constant, and introducing its value (39·0 Kg.C. units), the equation then becomes:

$$\frac{19{,}500}{T} + \log_e \frac{c_1^2}{c_2} = k.$$

The values for k calculated from our results are as follow:

T.	c_1.	c_2.	k.
1123°	0·9377	0·0623	20·01
1173	0·9778	0·0222	20·39
1223	0·9868	0·0132	20·24
1273	0·9941	0·0059	20·44
1323	0·9963	0·0037	20·32
1373	0·9985	0·0015	20·70
1473	0·9994	0·0006	20·65

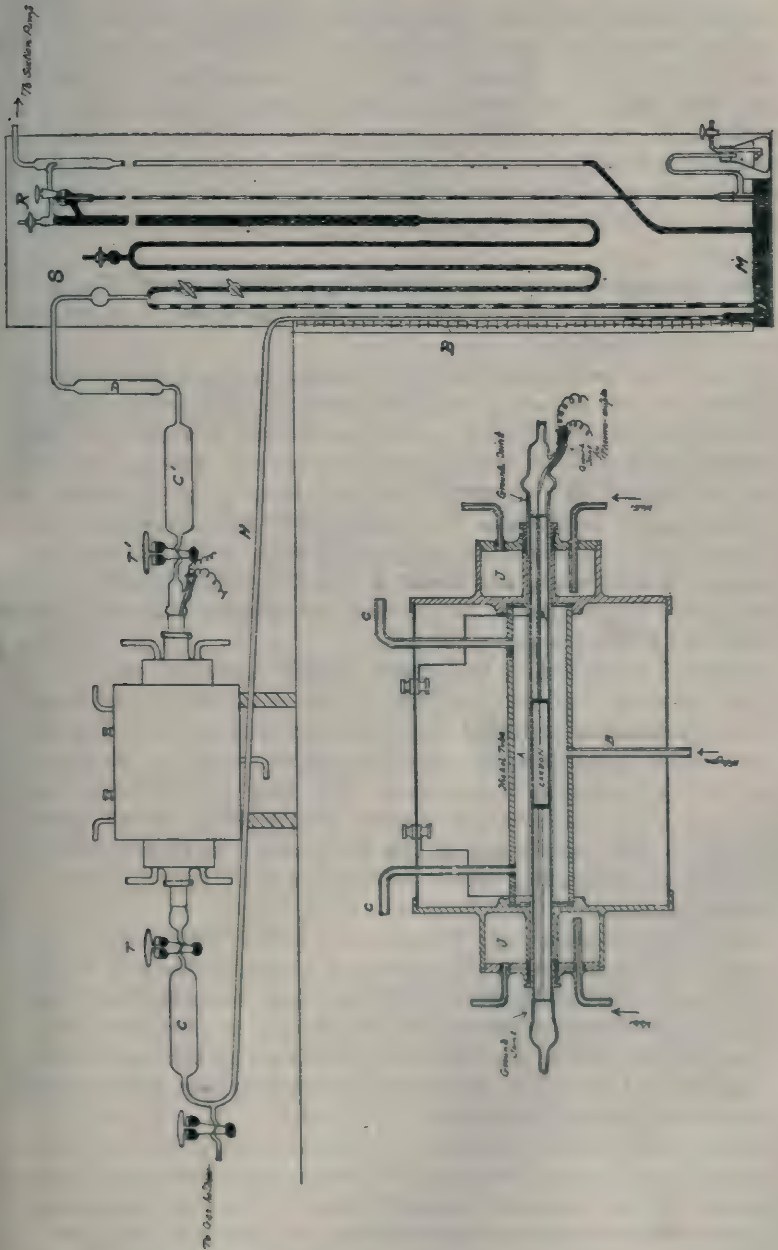
EXPERIMENTAL.

The Equilibrium Furnace.—In designing the equilibrium furnace, the two chief considerations were (*a*) the obtaining of a uniform temperature, and (*b*) the attainment of rapid cooling of the gases after they had left the zone of reaction, in order to "fix" the equilibrium. We had, moreover, to recognise the fact that at temperatures above 1000° both porcelain and fused silica or quartz tubes, such as we intended to employ for the reaction vessel, become slightly porous to gases.

The construction of the furnace, which was made for us by Messrs. C. W. Cook and Co., at the University Engineering Works, Manchester, is shown in Fig. 1. It consists essentially of a glazed Berlin porcelain tube, 51 cm. long and of 28 mm. external and 20 mm. internal diameter, wound with platinum wire, through which an electric current can be passed. The winding is arranged so as to give a uniform temperature throughout the central portion of 12 cm., and is carried on either side close up to the gunmetal water-jackets, *J*, being insulated from them by thin disks of porcelain. By winding the coils closer near each end than along the rest of the tube, we are able, when a fairly rapid stream of water is passing through the jackets, to obtain a sudden reduction in the temperature of the tube from 1000° in the central uniform portion to 400° or less within a distance of 1·5 cm., while the temperature falls to below 150° within a distance of 5 cm.

This result is not attained solely as the effect of water-cooling and increasing the length of resistance wire at the ends, but is in part due to the double-jacketing arrangement, *A*, which is intended primarily to avoid any error due to porosity of the porcelain tube at high temperatures. A nickel tube, 22 cm. long and of 7·1 cm. external and 5·7 cm. internal diameter, is fixed coaxially with the

FIG. 1.


To Suction Pump
R
S
M
B
D
C'
T'
H
C
T
To Gas Holder
Ground Joint
Ground Joint to Thermo-couple
J
C
Nickel Tube
A
CARBON
B
Gas
Ground Joint

porcelain tube, and through the annular space a slow stream of dry nitrogen is passed. The nitrogen, prepared by Harcourt's method, enters under a slight pressure through the central tube *B*, and issues at *C*, *C* through wash-bottles containing concentrated sulphuric acid. The passing of this stream of dry nitrogen, in addition to ensuring that no oxygen or water vapour enters the porcelain tube if it becomes porous at high temperatures, causes a more uniform distribution of heat throughout the length of the furnace, an effect which is enhanced by the position of entrance of the gas.

The furnace tubes are surrounded by a thick layer of kieselguhr to prevent loss of heat by radiation, and the whole is encased in a jacket of sheet iron.

The carbon used throughout this research has been wood charcoal purified by first digesting with concentrated hydrochloric acid (in a bolt-head flask fitted with a reflex condenser) to remove the ash; washing with distilled water; and subsequently heating at 1000° in a stream of dry chlorine, washing, heating in a stream of hydrogen, and finally in a vacuum at 1000° for forty-eight hours. It is crushed and sieved so as to pass through a 10-mesh sieve and remain on a 30-mesh, and about 6 grams are then loosely packed into a thin tube of quartz, 12 cm. long and open at both ends, which slides easily into the porcelain tube.

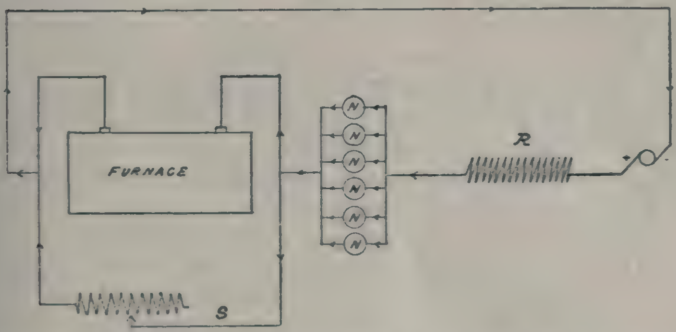
After the insertion of the quartz sheath containing the carbon, a plug of silica, 16·5 cm. long and 1·9 cm. in diameter with a hole 3 mm. in diameter drilled through the centre, is introduced at each end. These plugs serve to keep the carbon surface in position in the zone of constant temperature, but they are intended more especially to cause the stream of gases, after passing over the heated carbon, to pass rapidly out of the tube, and thus ensure that the equilibrium determined shall be that of the experimental temperature recorded.

The Measurement of Temperature.—The temperatures are measured by means of a platinum and platinum-rhodium thermocouple, and recorded by one of the Cambridge Scientific Instrument Company's "Thread-Recorders." The couple is embedded in the middle of the carbon, the leads being insulated by thin quill tubing of quartz, and the whole enclosed in a sheath of thin quartz, which passes easily through the bore of the plug *P*.

Some little difficulty was at first experienced in maintaining a constant temperature, owing to fluctuations in the voltage of the electric current supplied to the furnace. Since the experiments extended continuously over several days, or, in some cases, several weeks, personal attention was found to be impossible, and a means had to be devised of automatically regulating the voltage. The method finally employed, for the suggestion of which we are indebted to Mr. E. Muller, of the Cambridge Scientific Instrument Company, is as follows.

The voltage of the main current is first cut down by the large resistance, *R* (Fig. 2), to within a small margin of that required to obtain the experimental temperature in the furnace. It then passes through the Nernst lamp steadying resistances, *N*, of which a sufficient number are arranged in parallel to allow the requisite quantity of current to pass round the circuit. These steadying resistances take as their normal current 1 ampere at 15 volts, whilst the furnace, when hot, takes about 3 amperes. The exact number that are required to ensure perfect regulation and automatic adjustment of the voltage across the furnace terminals depends on the experimental temperature employed; there must be a sufficient number to ensure that the spirals of fine iron wire within the exhausted globes of each shall glow a dull red without becoming overheated; for they depend for their action on the change in electrical resistance that occurs in iron wire at a temperature of about 775°.

FIG. 2.



After passing through the Nernst lamp resistances, the current is divided, part going through the furnace, and part through the shunt, *S*, containing a rheostat. About equal quantities of current pass through the furnace and the shunt. The final adjustment of the voltage across the furnace to that required to obtain a given temperature is made by means of the rheostat in the shunt, the alteration of which does not interfere with the main current, since the whole of it passes through the Nernst lamp resistances.

This method has proved eminently satisfactory, the experimental temperature being maintained without any serious fluctuations continuously during several weeks.

General Arrangement of Apparatus.—The reacting gases are circulated without interruption over the heated carbon until equilibrium is attained. The general form of the circulation apparatus is that designed by one of us in conjunction with W. A. Bone for the investigation of the slow combustion of hydrocarbons (Trans., 1903, **83**, 1074).

The porcelain tube containing the carbon carries a ground glass joint at each end held firmly in position by strong springs. These joints make connexion on either side, through the mercury-cup taps T, T' (Fig. 1), with the cylindrical vessels C, C', each of 200 c.c. capacity. These vessels mainly determine the capacity of the apparatus, and are cylindrical in form in order to allow of being heated to drive off any traces of gas that may have a tendency to stick to the glass.

On the right-hand side, connexion is made, through the calcium chloride drying-tube D, to the head of the Sprengel pump S. On the left is fused a long tube of wide bore, which passes horizontally across the front of the furnace and is then bent downwards at right angles, forming a manometric tube, which stands over the delivery-tube of the Sprengel pump in the mercury trough M. A short T-piece near the left-hand cylinder, closed by a mercury-cup tap, serves for the introduction of the gas.

With the exception of the ground joint connexions to the porcelain tube, the apparatus is of fused glass throughout.

The gases are drawn, by means of the automatic Sprengel pump, through the furnace, and delivered under mercury in the trough M into the manometric tube B, whence they return along the horizontal tube H to the cylinder C, and are again drawn forward through the furnace. The automatic Sprengel pump, the general construction of which is described in the paper referred to above (*loc. cit.*, p. 1079), is actuated by suction produced by a double-acting Geryk pump driven by an electric motor, and is so arranged that the head of mercury in the reservoir R allows of the gases being circulated at atmospheric pressure.

The total volume of the apparatus, measured at 0°, is 570 c.c.; that of the packed porcelain tube 96 c.c.

The Gas Analyses.—The carbon dioxide was prepared by dropping boiled concentrated sulphuric acid from a separating funnel into a boiled solution of sodium carbonate contained in an Erlenmeyer flask. The gas evolved was passed through two sulphuric acid worms, and collected in a glass gas-holder containing concentrated sulphuric acid, over which it was stored for two weeks before being used for an experiment.

The carbon monoxide was prepared from sodium formate, made into a stiff paste with distilled water, by the action of concentrated sulphuric acid. It was washed through two worms containing potassium hydroxide solution, and stored over sulphuric acid in the same manner as the carbon dioxide.

The gases remaining after an experiment were analysed volumetrically in a Bone and Wheeler gas analysis apparatus over mercury, from 200 to 300 measures of gas being taken for an analysis. Carbon dioxide was estimated by absorption with as small a quantity of aqueous potassium hydroxide as possible, or when only small quantities were present, by absorption with a concentrated solution of barium hydroxide. Carbon monoxide was absorbed by an ammoniacal solution of cuprous chloride, prepared by passing ammonia gas into distilled water containing the freshly precipitated cuprous chloride in suspension until the latter was dissolved. A little ammonium chloride was added to the solution as thus prepared to reduce the tension of ammonia vapour. The gas was treated twice with small quantities of this solution, and afterwards washed with dilute sulphuric acid.

Any residue (which never amounted to more than 2 per cent. of the total gas) was afterwards exploded with a measured volume of air and oxygen, to which a few c.c. of pure electrolytic gas were added. Any contraction in volume after explosion, or after absorption with potassium hydroxide, was then determined. A trace of hydrogen due to insufficient drying of the gases, or to moisture in the circulation apparatus, was detected in several experiments the results of which were discarded.

Method of Conducting an Experiment.—The apparatus having been thoroughly exhausted, the glass being heated in a large blowpipe flame to drive off the last traces of air, the carbon dioxide (or monoxide) is introduced in such quantity that when the reaction is complete the gases shall be as nearly as possible at atmospheric pressure. As a preliminary to a series of experiments, a certain quantity of carbon dioxide is introduced to the carbon heated to 1000° and allowed to circulate for several days. The resulting gases are then pumped out, and the furnace brought to the experimental temperature. This preliminary treatment serves to remove any traces of water-vapour that still remain in the apparatus; it was in the gases resulting from such experiments that we were able to detect traces of hydrogen.

In the experiments proper the gases are allowed to circulate for twenty-four hours after the volume, as indicated by a scale fixed behind the manometric tube, has ceased to change. The reaction tube is then shut off from the rest of the apparatus, and samples are withdrawn for analysis.

Results of Experiments.

The results of our experiments can best be expressed in tabular form as follow:

Experiment number.	Temperature.	Duration of heating, hours.	Composition of resulting gases (calculated as nitrogen-free mixture).	
			CO_2.	CO.
E 14	850°	240	6·23	93·77
E 9	900	180	2·22	97·78
E 16	950	144	1·32	98·68
E 4	1000	48	0·59	99·41
E 18	1050	48	0·37	99·63
E 5	1100	48	0·15	99·85
E 6	1200	48	0·06	99 94

In addition, we have made two attempts to attain equilibrium at a temperature of 800° with the circulation apparatus, but have abandoned the experiments after they had continued for six weeks without showing signs of coming to a conclusion, 20 per cent. of carbon dioxide still remaining after that time.

Boudouard, in the reduction of carbon dioxide by wood charcoal without the presence of a catalyst, states that equilibrium was attained in his experiments after six hours' heating at 800° and after twelve hours' heating at 650°, the percentages of carbon dioxide remaining in equilibrium being 6·3 and 61·5 per cent. respectively at the two temperatures. The volume of his apparatus was only from 12 to 15 c.c. as against our 570 c.c., but we do not think that this fact is sufficient to explain the marked discrepancy between our results, since we used a correspondingly larger quantity of carbon surface. In another series of experiments that we are making on the rate of reduction of carbon dioxide by wood charcoal at different temperatures, we have been unable to obtain a disappearance of carbon dioxide of more than 0·7 per cent. after 122 hours' heating at 700°.

All our experiments recorded above have been made starting with an initial concentration of 100 per cent. carbon dioxide; for the rate at which the reverse reaction proceeds was too slow to enable us to attain equilibrium in a reasonable time without the presence of a catalyst, the use of which we wished to avoid.

The relative rates of the two reactions during the initial stages are well shown in the experiments recorded below. A temperature of 850° was chosen as being that at which the reduction of carbon dioxide by carbon was fairly rapid, and the dissociation of carbon monoxide readily appreciable.

The rates of the reactions are calculated, by means of the relation

$$\frac{1}{t}\log\frac{C_o}{C_t} = k,$$

from the partial pressures (concentrations) of the carbon dioxide at different time intervals in experiment R 13, and from the partial pressures of the carbon monoxide in experiment R 15:

Experiment R 13.

$CO_2+C=2CO$. Temperature 850°.

Time. (Unit=1 hour).	*P*. at 0°.	P_{CO_2}.	k_{CO_2}.
0	258·6	257·6	—
1	292·3	224·9	0·0590
2	317·8	199·4	0·0555
4	356·3	160·9	0·0511
6	389·0	128·2	0·0505
8	415·8	101·4	0·0506
12	439·5	77·7	0·0434

Experiment R 15.

$2CO=CO_2+C$. Temperature 850°.

Time. (Unit=1 hour).	*P*. at 0°.	P_{CO}.	k_{CO}.
0	463·0	453·7	—
24	459·2	446·1	0·00030
48	453·9	435·5	0·00037
72	452·1	431·9	0·00030
96	448·0	423·7	0·00031
120	447·2	422·1	0·00026

It will thus be seen that the reduction of carbon dioxide by carbon takes place at 850° at a speed 166 times as great as the dissociation of carbon monoxide at the same temperature.

We may incidentally draw attention to the fact that the good agreement of the constant *k*, calculated from the expression $\frac{1}{t}\log\frac{C_0}{C_t}$ for a unimolecular reaction, points to both reactions being essentially surface phenomena; the rate of reduction of carbon dioxide and the rate of dissociation of carbon monoxide both varying directly with the partial pressure of the gas. It is our intention to discuss this question more fully when we have concluded a research, on which we are at present engaged, on the relative rates of reaction between carbon dioxide, carbon monoxide, oxygen, and carbon at different temperatures.

This work has been undertaken in connexion with the experiments now being carried out by the Mining Association of Great Britain on coal-dust explosions. We are extending it to the investigation of the influence of pressure on the equilibrium ratio.

ALTOFTS.

CCXXVII.—*The Morphotropic Relationships between Silicon and Carbon Compounds of Corresponding Compositions.*

By George Jerusalem.

Carbon occupies an altogether unique position amongst the elements in crystallographic as well as in chemical respects; although large numbers of compounds of the elements of group IV of the periodic classification have been crystallographically examined, no case has been yet observed in which a carbon atom is isomorphously replaced by one atom of any other element. It is true that both carbon tetraiodide and silicon tetraiodide crystallise in the cubic system, but, since the crystal class is known in neither case, the information requisite for deciding as to whether these two compounds are isomorphous is lacking. Isomorphism might be expected as between the metallic carbonates and metasilicates, but although comparison is possible in a number of cases, no instance is on record in which silicon replaces carbon without profound modification of the crystalline form; thus lithium carbonate, Li_2CO_3, is monosymmetric with $a:b:c=1·672:1:1·244$, $\beta=114°25'$ (Mallard, *Zeitsch. Kryst. Min.*, 1894, **23**, 483), whilst lithium metasilicate, Li_2SiO_3, is rhombohedral with $a:c=1:0·6681$ (Friedel, *Zeitsch. Kryst. Min.*, 1903, **37**, 204). Comparison of the crystalline forms exhibited by the carbonates of the bivalent metals with those of the compounds $CaSiO_3$, $MgCa(SiO_3)_2$, $MgSiO_3$, $MnSiO_3$, $MgTiO_3$, $MnTiO_3$, and $FeTiO_3$, fails to reveal any isomorphous relationship between the carbonates and the latter compounds. Further, the observation that carborundum, CSi, is a stable substance dissimilar in crystalline form from either component element does not favour the view that the two elements are isomorphous.

Whilst a considerable amount of evidence, such as the above, indicates that carbon is crystallographically quite unique, it is noteworthy that ample evidence is available to show that silicon is displaceable by many bivalent elements without considerable change in crystalline form.

From a discussion of the crystal data available for carbon and silicon compounds, Barlow and Pope have been led to attribute the crystallographic—and also chemical—dissimilarity to a difference in the fundamental valencies of these two elements (Trans., 1908, **93**, 1554); carbon thus stands alone as the only element exhibiting the fundamental valency of four, whilst silicon and many other elements are fundamentally bivalent. Owing to the comparative ease with which, during the last few years, it has become possible to exhibit the relation between chemical constitution and crystalline form, the question of the relative fundamental valencies of silicon and carbon has become one of great importance; the work described in the present paper was undertaken as a step towards the solution of the problem involved.

A study of the crystal data already available for corresponding silicon and carbon compounds indicates clearly that the two elements exercise such different morphotropic effects that few positive results could be hopefully anticipated unless some condition, hitherto unconsidered, were introduced for the purpose of accentuating such crystallographic similarity of function as may exist between silicon and carbon. The directing condition, thus indicated as desirable, is found in the rule discovered empirically by Tschermak (*Tsch. Min. Mitt.*, 1903, **22**, 393; *Ann. Reports*, 1908, **5**, 263) that, in the crystalline form of a compound substance, the principal axes of symmetry tend to express numerically the atomic composition of the molecule; thus, if three similar atoms are present with others in the molecule of a particular substance, the crystalline form of the compound will, in the majority of cases, include a three-fold axis of symmetry. Since crystal structures are now regarded as close-packed assemblages of atomic domains, a compound containing *n* identically located atoms, or groups of atoms, in the molecule would tend to exhibit a particular element of symmetry displaying an *n*-fold repetition; Tschermak's empirical rule has thus now acquired theoretical significance and, simultaneously, a concrete meaning. The rule may be conveniently applied to the purpose of accentuating any possible morphotropic relationship between two elements *a* and *b*, by preparing two substances containing in the molecule three large atomic groups or radicles associated with an *a* and *b* atom, respectively, of a unique kind; any morphotropy exhibited as between *a* and *b* should then be easily traced by goniometric examination.

This particular development of the new mode of regarding crystal structure is applied in the present paper to the examination of tribenzyl and triphenyl derivatives of silicol and carbinol; the introduction of three benzyl or phenyl groups into the molecule is, of course, intended to secure the presence of a trigonal axis of symmetry and to ensure that the silicon and carbon analogues shall to a very great extent exhibit identical marshalling of their component atoms.

Tribenzylsilicol, $(C_6H_5{\cdot}CH_2)_3Si{\cdot}OH$.

A supply of this substance was kindly provided by Prof. F. S. Kipping, and melted at 106°, as stated by Dilthey (*Ber.*, 1905,

38, 4136). On slow evaporation of its solution in a mixture of chloroform and petroleum boiling at 70°, it was obtained in small, lustrous crystals suitable for measurement; the form {001} is the largest, and {100}, {101}, and {111}, although smaller, are well developed. The pyramid, {122}, is always very small but quite brilliant; no distinct cleavage was observed, but, as the faces of {111} are always much larger at one end of the *c*-axis, and as the faces of {122} are only observed at the same end of this axis, the substance is probably hemimorphous. No confirmation of the hemimorphism was obtained by the study of the etch-figures produced by the action of alcohol on faces of the form {001}.

Crystalline form: Orthorhombic.

$a : b : c = 1\cdot7214 : 1 : 2\cdot1384$.

Forms observed: {100}, {001}, {101}, {111}, and {122}.

The following angular measurements were obtained:

Angles.	Number of observations.	Limits.	Mean.	Calculated.
$111 : \bar{1}11$	16	55° 2′—55°49′	55°30′20″	—
$111 : 11\bar{1}$	14	43 46 —44 15	44 1 50	—
111 : 100	33	61 31 —62 54	62 13 0	62°14 50″
101 : 001	13	50 59 —51 35	51 13 30	51 10 0
001 : 122	4	65 31 —66 6	65 53 0	65 48 50
101 : 100	9	38 26 —39 6	38 47 0	38 50 0
$122 : \bar{1}22$	1	48 23	48 23 0	48 22 20
111 : 001	9	67 43 —68 17	68 1 50	67 59 0
101 : 111	4	53 16 —53 27	53 19 10	53 17 10
100 : 122	10	74 51 —75 20	75 7 50	75 15 30

It is very interesting to note that, although the substance does not exhibit a trigonal axis of symmetry as would be anticipated from Tschermak's empirical rule, it possesses a pseudo-trigonal axis, as would be expected from the interpretation of the rule and the molecular composition in accordance with Barlow and Pope's method. Thus, a crystal presenting trigonal symmetry, referred to rectangular axes, would exhibit as one axial ratio the value $1 : \sqrt{3} = 1 : 1\cdot7321$, whilst an almost identical ratio, $b : a = 1 : 1\cdot7214$, is actually observed on the crystals of tribenzylsilicol; the pseudo-trigonal nature of the crystal structure is thus apparent. It will be seen later that all the substances described below, in which three large groups are present in the molecular complex, conform to the same rule, and betray the presence of a trigonal or a pseudo-trigonal axis, with the possible exception of triphenylsilicol, of which the low crystal symmetry would naturally obscure the pseudo-trigonal character.

Taking the valency volume of silicon as two, that of tribenzylsilicol is $W = 110$, and the equivalence parameters are obtained as:

$$x : y : z = 5\cdot3418 : 3\cdot1032 : 6\cdot6358.$$

The density of the crystalline substance was determined by Retgers' floating method in barium mercuri-iodide solution as $d = 1{\cdot}1772$, whence the molecular volume, $V = 270{\cdot}66$; the quotient, $R = V/W = 2{\cdot}4605$, and the molecular distance ratios are calculated as:

$$\chi : \psi : \omega = 7\ 2116 : 4{\cdot}1894 : 8{\cdot}9586.$$

Tribenzylcarbinol, $(C_6H_5{\cdot}CH_2)_3C{\cdot}OH$.

This substance was prepared by the method given by Klages and Heilmann (*Ber.*, 1904, **37**, 1456), and was obtained in crystals suitable for goniometric measurement by spontaneous evaporation of its solution in a mixture of chloroform and petroleum. The crystals so closely resemble those of the preceding compound that no separate description is necessary.

Crystalline system: Orthorhombic.

$a : b : c = 1{\cdot}7166 : 1 : 2{\cdot}1574.$

Forms observed: {100}, {001}, {101}, {111}, and {122}.

The following angular measurements were obtained:

Angles.	Number of observations.	Limits.	Mean.	Calculated
100 : 111	26	61°52′—62°20′	62° 8′50″	—
001 : 111	22	68 0 —68 17	68 9 20	—
001 : 101	10	51 18 —51 37	51 26 50	51°28′10″
100 : 101	13	38 21 —38 44	38 32 50	38 31 50
111 : $\bar{1}11$	12	55 32 —55 51	55 37 10	55 42 20
111 : $11\bar{1}$	13	43 31 —44 1	43 40 20	43 41 20
111 : $\bar{1}1\bar{1}$	16	53 9 —53 36	53 20 50	53 19 30
100 : 122	12	74 51 —75 26	75 9 40	75 12 0
001 : 122	6	65 57 —66 7	66 2 10	65 59 20

The development of the faces indicates hemimorphous development as in the case of the corresponding silicol; the etch-figures obtained do not reveal hemimorphism. The axial ratios calculated show that the substance is very closely related morphotropically to the corresponding silicol, and the present observations constitute the first published evidence of morphotropy as between these two elements. The equivalent parameters are calculated as:

$$x : y : z = 5{\cdot}3482 : 3{\cdot}1156 : 6{\cdot}7215, \text{ with } W = 112.$$

The density of the crystals was determined as $d = 1{\cdot}1869$, whence the molecular volume, $V = 258{\cdot}99$, and the quotient, $R = V/W = 2{\cdot}3124$. The molecular distance ratios are therefore:

$$\chi : \psi : \omega = 7{\cdot}0724 : 4{\cdot}1200 : 8\ 8885.$$

Tribenzylmethyl Chloride, $(C_6H_5{\cdot}CH_2)_3CCl$.

This substance was prepared by the method given by Schmerda (*Monatsh.*, 1909, **30**, 390), and exhibited the properties described by him; it separates from its acetone solution in very small but quite brilliant rhombohedron-shaped crystals.

Crystalline system: Rhombohedral. Trapezohedral-tetartohedral class.

$a : c = 1 : 0{\cdot}3700$.

Forms observed: $\{2\bar{1}\bar{1}0\}$ and $\{10\bar{1}1\}$.

The following angular measurements were obtained:

Angles.	Number of Observations.	Limits.	Mean.	Calculated.
$2\bar{1}\bar{1}0 : 10\bar{1}1$	41	70° 0′—70°22′	70° 6′20″	—
$10\bar{1}1 : 0\bar{1}11$	18	39 34 —40 0	39 49 20	39°47′20″

The evidence that the crystals belong to the trapezohedral-tetartohedral class represented by quartz and cinnabar is, first, that the alternate faces of the form $\{2\bar{1}\bar{1}0\}$ are very different in size, and, secondly, that the etch-figures produced on these faces by the action of benzene are asymmetric with respect to the hexagonal planes of symmetry normal to the faces. A good cleavage is observed parallel to the form $\{2110\}$.

In order that the crystal form may be compared with those of the preceding compounds, it must first be stated with respect to the alternative hexagonal system and then referred to rectangular axes and the value, c/a, multiplied by five; the axial ratios are thus obtained in the form:

$a : b : c = 1{\cdot}7321 : 1 : 2{\cdot}1364$, and the equivalence parameters as:
$x : y : z = 5{\cdot}3656 : 3{\cdot}0977 : 6{\cdot}6180$, with $W = 110$.

The use of the factor five in the multiplication of the ratio c/a is naturally justified by the very close similarity which the equivalence parameters of the three above substances exhibit after the multiplication has been performed in the case of tribenzylmethyl chloride.

Triphenylsilicol, $(C_6H_5)_3Si{\cdot}OH$.

Triphenylsilicol was prepared by Dilthey and Eduardoff's method (*Ber.*, 1904, **37**, 1140), and showed the properties described by these authors; the best crystals were obtained from solutions in mixtures of chloroform and petroleum, but even these were poor, and scarcely suitable for goniometric examination. The forms $\{100\}$, $\{010\}$, and $\{001\}$ show the largest faces, and are about equally well developed; $\{111\}$ and $\{1\bar{1}1\}$ are very poorly developed, and unsatisfactory in character.

Crystalline system: Anorthic.

$a : b : c = 2{\cdot}144 : 1 : 1{\cdot}331$, $\alpha = 59°30'$, $\beta = 113°29'$, $\gamma = 84°11'$.

Forms observed: $\{100\}$, $\{010\}$, $\{001\}$, $\{111\}$, and $\{1\bar{1}1\}$.

The following angular measurements were obtained:

Angles.	Number of observations.	Limits.	Mean.	Calculated.
$100 : 001$	16	58° 1′—58°48′	58°20′50″	—
$\bar{1}00 : 010$	8	67 5 —67 46	67 25 0	—
$00\bar{1} : 010$	10	52 50 —53 29	53 6 10	—
$\bar{1}00 : \bar{1}11$	9	64 10 —64 47	64 29 30	—
$\bar{1}11 : 001$	8	90 38 —91 18	90 57 40	—
$\bar{1}11 : 010$	7	41 0 —41 58	41 39 10	42°10′20″
$111 : 001$	5	61 56 —62 38	62 19 0	62 19 40
$111 : 010$	4	68 22 —68 53	68 36 30	69 2 20
$111 : 100$	2	58 57 —59 24	59 10 30	59 46 30

The density of the crystals was observed as $d = 1{\cdot}1777$, so that the molecular volume, $V = 234{\cdot}83$; the quotient, $R = V/W = 2{\cdot}5525$ No morphotropic relationship is immediately obvious between this and the previously described substances, and, since triphenylsilicol belongs to the anorthic system, the symmetry affords no indication as to the way in which a morphotropic relationship is to be sought; further, the ratio, V/W, is considerably larger than in the other cases referred to. It is consequently to be concluded that this silicol does not fall into line with the series now under discussion.

Triphenylcarbinol, $(C_6H_5)_3C{\cdot}OH$.

This substance has already been crystallographically examined by Groth (*Zeitsch. Kryst. Min.*, 1881, **5**, 479), who found it to be rhombohedral with $a : c = 1 : 0{\cdot}6984$. Measurable crystals were obtained from benzene solution, and these showed only the forms $\{10\bar{1}1\}$ and $\{11\bar{2}0\}$.

Crystalline system: Rhombohedral. $a : c = 1 : 0{\cdot}6975$.

The following angular measurements were obtained:

Angles.	Number of Observations.	Limits.	Mean.	Calculated.
$2\bar{1}\bar{1}0 : 10\bar{1}1$	13	56°46′—57°19′	57° 5′40″	—
$10\bar{1}1 : 0\bar{1}11$	5	65 35 —66 5	65 47 20	65°48′40″

In order to render the crystal form comparable with those of the tribenzyl compounds described above, the ratio c/a must be multiplied by three and referred to a rectangular system of axes. The following ratios are thus obtained:

$$a : b : c = 1{\cdot}7321 : 1 : 2{\cdot}0925.$$

$$x : y : z = 5{\cdot}1271 : 2{\cdot}9601 : 6{\cdot}1939;\ W = 94.$$

The density of the crystals was determined as $d = 1{\cdot}1884$, so that the molecular volume, $V = 218{\cdot}92$, and the quotient, $R = V/W = 2{\cdot}3289$. The molecular distance ratios are:

$$\chi : \psi : \omega = 6{\cdot}7960 : 3{\cdot}9236 : 8{\cdot}2100.$$

The value for R is slightly greater than that for tribenzylcarbinol, namely, 2·3124; this is in accordance with the indications obtained in the case of the picrates and styphnates. Aniline picrate gives an R value of 2·464, slightly greater than 2·433, the value for benzylamine picrate (Jerusalem. Trans., 1909, **95**, 1290).

For comparison with the above substances the following crystalline forms may be quoted. Triphenylmethane is described as orthorhombic by Hintze with $a:b:c=0·5716:1:0·5867$ (*Zeitsch. Kryst. Min.*, 1884, **9**, 546); on interchanging a and b, and multiplying the resulting value of c/b by two, the axial ratios become:

$$a:b:c=1·7495:1:2·0528.$$

ω-Bromotriphenylmethane, Ph_3CBr, was found to be hexagonal by Hintze (*loc. cit.*) with the value $a:c=1:0·7843$; on stating this ratio in the alternative hexagonal form as $a:c=1:0·6792$, multiplying c/a by three, and referring the ratio to rectangular axes, the values are obtained as:

$$a:b:c=1·7321:1:2·0376.$$

Triphenylacetic acid is monosymmetric (Groth, *Zeitsch. Kryst. Min.*, 1881, **5**, 483), and the axial ratios can be stated in the form $a:b:c=0·5646:1:0·6161$, $\beta=90°12'30''$ (Barlow and Pope, Trans., 1906, **89**, 1719). On treating these axial ratios in the manner adopted with triphenylmethane, namely, multiplying c/b by two, and then interchanging a and b, the values become:

$$a:b:c=1·7712:1:2·1824, \alpha=90°12'30''.$$

The additive compound of triphenylmethane and benzene, $(C_6H_5)_3CH,C_6H_6$, is rhombohedral with $a:c=1:2·5565$ (Hintze, *loc. cit.*); by referring this ratio to rectangular axes it becomes:

$$a:b:c=1·7321:1:2·5565.$$

A consideration of the axial ratios, molecular distance ratios, and equivalence parameters for the above substances shows, first, that although the morphotropic relationships are distinctly evident in the axial ratios, they are much more completely expressed by the equivalence parameters. Secondly, it is obvious that the molecular distance ratios, although not greatly dissimilar in the instances in which they have been determined, differ much more amongst themselves than do the equivalence parameters; the degree with which they correspond is, in fact, measured in the main by the degree of approximation of the respective values of $R=V/W$. In this, as in the majority of other cases, the molecular distance ratios lend themselves less fruitfully to the discussion of morphotropic relationships than do the equivalence parameters; the morphotropy must therefore be considered merely in the light of the equivalence parameters, and the axial ratios and molecular distance ratios may be disregarded.

The following table states the equivalence parameters of all the substances dealt with above, calculated from the sets of axial ratios finally adopted. In the case of tribenzylsilicol, it is convenient to state the equivalence parameters in accordance with the alternatives that Si = 2 and 4:

	x.	*y*.	*z*.		
1. $(C_6H_5\cdot CH_2)_3Si\cdot OH$	5·3418 :	3·1032 :	6·6358	*W* = 110	Si = 2
2. $(C_6H_5\cdot CH_2)_3Si\cdot OH$	5·3740 :	3·1219 :	6·6758	*W* = 112	Si = 4
3. $(C_6H_5\cdot CH_2)_3C\cdot OH$	5·3482 :	3·1156 :	6·7215	*W* = 112	
4. $(C_6H_5\cdot CH_2)_3CCl$	5·3656 :	3·0977 :	6·6180	*W* = 110	
5. $(C_6H_5)_3C\cdot OH$	5·1271 :	2·9601 :	6·1935	*W* = 94	
6. $(C_6H_5)_3CH$	5·1572 :	2·9479 :	6·0515	*W* = 92	
7. $(C_6H_5)_3CBr$	5·1358 :	2·9651 :	6·0416	*W* = 92	
8. $(C_6H_5)_3C\cdot CO_2H$	5·2384 :	2·9576 :	6·4546	*W* = 100	
9. $(C_6H_5)_3CH, C_6H_6$	5·2314 :	3·0203 :	7·7213	*W* = 122	

Considering the parameters 2 and 3, calculated on the basis that silicon and carbon both exhibit the fundamental valency 4, it is noticed that in passing from the silicol to the carbinol, the *x*-value diminishes by about one-half per cent., whilst the *z*-value increases by rather a larger fraction. If crystal structure is to be regarded as a question of close-packing, it is difficult to conceive that in the large tribenzylsilicol molecule the displacement of the silicon by a carbon atom of approximately the same valency volume four can lead, without change of symmetry, to such a notable change in dimensions of the packed structure; it seems thus indicated that carbon and silicon have not the same fundamental valency of four.

On considering next the values 1 and 3, calculated on the basis of Si = 2 and C = 4, it is seen that the differences for *x* and *y* are small, and that practically the whole weight of the displacement of silicon by carbon falls on the *z*-parameter, which thus changes by nearly 2 per cent.; this is in complete agreement with what would be anticipated by an increase of volume of one constituent atomic domain from 2 to 4. Such a substitution, provided that the mechanical operation of Tschermak's rule conserves the marshalling, could well lead to the expansion of the assemblage in one of the three rectangular directions of principal symmetry. An identical effect is, in fact, observed in operation in other cases, notably in the passage from tribenzylcarbinol to tribenzylmethyl chloride, where a similar change of valency volume by two units occurs as

		x.	*y*.	*z*.
2 and 3	Differences	0·0258	0·0063	0·0457
1 ,, 3	,,	0·0064	0·0124	0·0857
3 ,, 4	,,	0·0174	0·0179	0·1035
3 ,, 5	,,	0·2211	0·1555	0·5280
5 ,, 6	,,	0·0301	0·0122	0·1420
5 ,, 7	,,	0·0087	0·0050	0·1519
5 ,, 8	,,	0·1113	0·0025	0·1519
6 ,, 9	,,	0·0742	0·0724	0·6698

the result of the displacement of the hydroxyl group by the chlorine atom; here again small changes occur in the values of two dimensions, x and y, and most of the weight of the substitution is thrown on to the third or z-parameter, which alters by about 1·5 per cent.

These considerations suggest that silicon and carbon have not the same fundamental valency, but that, whilst that of carbon is four, that of silicon is two. The available evidence is, however, not sufficient in amount to enable such a decision to be arrived at with certainty, but it must be concluded that the quantitative evidence, just as in the case of the humite series, points to the value of 2 rather than 4 as representing the fundamental valency of silicon.

The table of differences quoted makes it clear that the passage from tribenzylcarbinol to triphenylcarbinol, differences 3 and 5, is accompanied by a marked contraction of the structure in all three rectangular directions, but that this effect is much more marked in the direction of the z-dimension than in those of x and y. From differences 5 and 6, and 6 and 7, it is seen that the substitution of the hydroxyl group in triphenylcarbinol by hydrogen or bromine affects the crystal structure almost entirely in the direction of the z-axis; this is precisely what takes place in the corresponding operation of passing from tribenzylcarbinol to tribenzylsilicol, in which the valency volume was diminished by two units on the view that $Si = 2$. The differences 5 and 8 show that the displacement of the hydroxyl group in triphenylcarbinol by carboxyl also produces a maximum effect in the z-dimension, although the dimension of x is also appreciably affected. The differences 6 and 9 indicate clearly that, in the passage from triphenylmethane to its addition compound with benzene, the dimensions of x and y are increased to an equal and small extent, whilst the main change in dimensions falls on the z-axis.

It is proposed to extend the application of Tschermak's rule to the investigation of morphotropy in later communications.

I desire to express my heartiest thanks to Prof. W. J. Pope, F.R.S., for having suggested this work, and for his kind help during its elaboration.

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CCXXVIII.—*Externally Compensated Tetrahydroquinaldine (Tetrahydro-2-methylquinoline) and its Optically Active Components.*

By William Jackson Pope and John Read.

The resolution of externally compensated tetrahydroquinaldine (tetrahydro-2-methylquinoline) into its optically active components was effected by Pope and Peachey (Trans., 1899, **75**, 1066) by crystallising its hydrochloride (two equivalents) with ammonium *d*-α-bromocamphor-π-sulphonate (one equivalent) in aqueous solution; the deposit consists of practically pure *l*-tetrahydroquinaldine *d*-α-bromocamphor-π-sulphonate. The *d*-tetrahydroquinaldine was isolated from the mother liquors by fractional crystallisation of the benzoyl derivative prepared from the separated crude *d*-base and subsequent hydrolysis of the pure benzoyl-*d*-tetrahydroquinaldine. The method thus briefly described affords an easy method for the preparation of *l*-tetrahydroquinaldine, but the isolation of the enantiomorphously related base is lengthy and difficult; in the present paper a method is described by means of which the two enantiomorphously related bases can be readily prepared in a state of high purity.

Externally Compensated Tetrahydroquinaldine.

This base was prepared, in the manner previously described, as a colourless oil, boiling at 196°/207·5 mm.; at the ordinary temperature it is a mobile liquid which shows no tendency to crystallise, and, on cooling in boiling liquid air, it solidifies to a hard, resinous material, which does not crystallise even after long exposure to the low temperature thus obtained. When, however, a few drops of the base are dissolved in ten times their volume of light petroleum, and the solution cooled in boiling liquid air, tetrahydroquinaldine crystallises out as a mass of white needles; on inoculating carefully purified externally compensated tetrahydroquinaldine with these crystals at the ordinary temperature, crystallisation at once sets in, and after the lapse of some hours the whole of the base becomes converted into a hard, crystalline mass.

It is thus evident that at the ordinary laboratory temperature externally compensated tetrahydroquinaldine is a supercooled liquid; no other method than the one above described has yet been found for causing the crystallisation. In all probability, the fact that crystallisation can only be started by such an uncommon method as that just described is responsible for the observation not having been previously made that the modification of tetrahydroquinaldine stable at the ordinary temperature is a crystalline one.

A specimen of externally compensated tetrahydroquinaldine, prepared from a sample of the hydrochloride which had been repeatedly crystallised from acetone, after having been caused to crystallise in the manner indicated, melted at 20·75°; after melting the crystalline mass, cooling it to 15°, and inoculating the liquid with the crystalline base, a standard thermometer immersed in the solidifying substance showed that the temperature rose to 20·75° during crystallisation. This may therefore be taken as the melting point of externally compensated tetrahydroquinaldine. It is interesting to note that on preserving a quantity of the crystalline material in contact with the liquefied substance at the laboratory temperature, the mass of minute crystals gradually becomes converted into several large rhombohedra; the latter grow to a diameter of four or five centimetres, and are very transparent, with highly plane faces. A good example is thus afforded of the well-known fact that the larger crystals present in contact with a solution tend to grow at the expense of the smaller ones (Curie, *Bull. Soc. Min. franç.*, 1885, **8**, 145).

Preparation of Ammonium d- *and* l-*α-Bromocamphor-π-sulphonates.*

For the preparation of the large quantities of ammonium *d*- and *l*-*α*-bromocamphor-*π*-sulphonates required in this and similar work, the sulphonation with chlorosulphonic acid (Kipping and Pope, Trans., 1895, **67**, 356) is inconvenient, and may be replaced by a slight modification of the method first used by these authors (Trans., 1893, **63**, 577). A mixture of fuming and 100 per cent. sulphuric acids is made of such concentration that *α*-bromocamphor dissolves in it to a deep amber-coloured solution, and is not precipitated by pouring on to ice; the concentration of the acid used requires careful adjustment, and a suitable concentration was found to have the density 1·865 at 15°, and to consist of 200 c.c. of 100 per cent. sulphuric acid with 75 c.c. of 65 per cent. sulphur trioxide. This quantity of acid, cooled to the ordinary temperature, readily dissolves 95 grams of *d*-*α*-bromocamphor, and simultaneously the temperature rises to about 50°. After agitation for half a minute, the mixture is poured through a large funnel filled with crushed ice, when an insignificant separation of unchanged bromocamphor occurs; if the acid used is too concentrated, the sulphonation product suddenly carbonises with evolution of torrents of sulphur dioxide. It is convenient to sulphonate a kilogram of *d*-*α*-bromocamphor in quantities of 100 grams at a time, and almost to neutralise the diluted solution with milk of lime, completing the neutralisation with calcium carbonate; the solution is then run through a filter press, the filtrate treated with ammonium carbonate in the usual manner, again filtered, and the filtrate evaporated to crystallisation in large copper pans. The small amounts of copper which pass into solution are precipitated by ammonium sulphide; care should be taken that the lime, calcium carbonate, and water used are free from chlorides, as the presence of ammonium chloride hinders the crystallisation of the ammonium bromocamphorsulphonate.

The following determinations of rotatory power were made in aqueous solutions at 22° in 4-dcm. tubes with ammonium salts which had been carefully purified by repeated crystallisation from water:

	Ammonium *d-α-Bromocamphor-π-sulphonate.*			Ammonium *l-α-Bromocamphor-π-sulphonate.*		
	2·0439 grams in 50 c.c.			2·0130 grams in 50 c.c.		
	Na(*D* line).	Hg(yellow).	Hg(green).	Na(*D* line).	Hg(yellow).	Hg(green).
α	+13·94°	+14·72°	+17·30°	−13·62°	−14·47°	−16·97°
$[\alpha]$	+85·25	+90·02	+105·80	−84·58	−89·85	−105·38

Mean values: $[M]_D$ 278·69°; $[M]_{Hg\,(yellow)}$ 295·17°; $[M]_{Hg\,(green)}$ 346·55°.

The mean rotatory dispersions calculated from the above values are, for $\mathrm{Hg}_{(green)}/\mathrm{Na}_{(yellow)} = 1{\cdot}243$, and for $\mathrm{Hg}_{(yellow)}/\mathrm{Na}_{(yellow)} = 1{\cdot}059$; these constants are appreciably smaller than the corresponding ones for the camphor-β-sulphonic ions (Pope and Gibson, this vol., p. 2213). The values for the rotatory power for the *D*-line compare well with those determined by Kipping and Pope (Trans., 1893, **63**, 589), namely, $[\alpha]_D$ +84·78° and $[M]_D$ +278·25°.

By treating the ammonium salts with baryta as previously described (Pope and Peachey, Trans., 1898, **73**, 893), solutions of the pure optically active acids can be obtained. The silver α-bromocamphor-π-sulphonates are easily obtained by saturating the solutions of the acids with silver hydroxide, filtering, and evaporating to crystallisation; this method is far more convenient than the one recommended by Meisenheimer (*Ber.*, 1908, **41**, 3973).

Resolution of Externally Compensated Tetrahydroquinaldine.

On treating racemic tetrahydroquinaldine hydrochloride with rather less than half an equivalent of ammonium *d*-α-bromocamphor-π-sulphonate, as already described (Trans., 1899, **75**, 1066), the greater part of the *l*-base separates as the sparingly soluble *l*-tetrahydroquinaldine *d*-α-bromocamphor-π-sulphonate; the latter salt is obtained in a state of high purity by crystallisation from alcohol. The mother liquors, containing the whole of the *d*-base, are then treated with sodium hydroxide, the base separated, and distilled;

the rotatory power of the distillate is then determined, and the percentage of *d*-base calculated; in general, about 80 per cent. of *d*-base is present. This base is next dissolved in the requisite amount of dilute hydrochloric acid, and to the hot solution is added ammonium *l*-α-bromocamphor-π-sulphonate; the proportion of the latter used is about 2 per cent. less than the quantity equivalent to the *d*-tetrahydroquinaldine present. Crystallisation does not ordinarily occur spontaneously, but may be induced by inoculation with a little crystalline *d*-tetrahydroquinaldine *l*-α-bromocamphor-π-sulphonate; the latter is readily obtained by evaporating a few drops of the solution to dryness, and rubbing the residue with ether. After inoculation, crystallisation takes place with considerable rise in temperature, and almost the whole of the *d*-base separates as the salt of the optically active acid; the salt is purified by crystallisation from boiling alcohol, and its physical properties correspond with those of the enantiomorphously related salt.

The base extracted from the final mother liquors consists mainly of *l*-tetrahydroquinaldine, which may be separated by again treating with ammonium *d*-α-bromocamphor-π-sulphonate in hydrochloric acid solution. The practically quantitative separation of the externally compensated tetrahydroquinaldine into its optically active components is thus effected.

l-(d-)*Tetrahydroquinaldine* d-(l-)*α-Bromocamphor-π-sulphonate.*

These salts, which crystallise in long, colourless needles, melting at 218—220°, exhibit distinct mutarotation in absolute alcoholic solution, but since the solutions, which are at first colourless, rapidly become brown, no trustworthy quantitative determinations of the mutarotation have yet been made. The observed values of the specific rotatory powers in 0·8 per cent. alcoholic solutions at 20° were:

$[\alpha]_D$ 37·0° to 41·4°, $[\alpha]_{Hg\ (yellow)}$ 39·2° to 43·0°, and $[\alpha]_{Hg\ (green)}$ 49·5° to 52·3°.

The solutions in water remain colourless, and no mutarotation was observed; the following values were obtained in 4-dcm. tubes at 17°:

	l-*Base*, d-*Acid*.			d-*Base*, l-*Acid*.		
	0·2118 gram in 30 c.c.			0·2034 gram in 30 c.c.		
	Na(*D* line).	Hg(yellow).	Hg(green).	Na(*D* line).	Hg(yellow).	Hg(green).
α	+0·91°	+0·96°	+1·14°	−0·87°	−0·92°	−1·09°
[α]	+32·22	+33·99	+40·37	−32·08	−33·92	−40·19

Mean values: $[M]_D$ 147·34°; $[M]_{Hg\ (yellow)}$ 155·61°; $[M]_{Hg\ (green)}$ 184·60°.

The rotatory dispersions calculated from the above values are, for $Hg_{(green)}/Na_{(yellow)}$ = 1·253, and for $Hg_{(yellow)}/Na_{(yellow)}$ = 1·056.

l- *and* d-*Tetrahydroquinaldine.*

The optically active bases were obtained by treating the above-described salts with alkali, and distilling the separated oil under diminished pressure. On cooling in boiling liquid air, they solidify to colourless resins, which show no tendency to crystallise; when a few drops of one of the active bases are dissolved in light petroleum and cooled in boiling liquid air, crystallisation occurs, but the crystalline material thus obtained does not cause the crystallisation of the *d*- or *l*-base when used for inoculation at any temperature which could be established. It thus appears that the optically active tetrahydroquinaldines crystallise at a temperature far below the ordinary one, whilst the racemic substance crystallises at 20·75°; a somewhat similar case is presented by the active and inactive methyl methoxysuccinates (Purdie and Neave, this vol., p. 1518).

The following determinations of rotatory power were made in 1-dcm. tubes, and the formula deduced by Pope and Peachey (Trans., 1899, **75**, 1114) as connecting the density and temperature of the bases was used in calculating the specific rotatory powers:

d-*Tetrahydroquinaldine* at 16°.

	Na*D* (line).	Hg(yellow).	Hg(green).
α	+61·13°	+63·66°	+71·85°
[α]	+59·79	+62·26	+70·27

l-*Tetrahydroquinaldine* at 20°.

	Na(*D* line).	Hg(yellow).	Hg(green).
α	−61·20°	−63·80°	−71·97°
[α]	−60·04	−62·59	70·61

The mean rotatory dispersions are, for $\mathrm{Hg}_{(\mathrm{green})}/\mathrm{Na}_{(\mathrm{yellow})} = 1{\cdot}176$, and for $\mathrm{Hg}_{(\mathrm{yellow})}/\mathrm{Na}_{(\mathrm{yellow})} = 1{\cdot}042$.

The purest specimen of *l*-tetrahydroquinaldine obtained by Pope and Peachey gave the specific rotatory power $[\alpha]_D$ −58·12°, which is slightly lower than the values now recorded. Ladenburg, who resolved the externally compensated base by crystallisation with tartaric acid, obtained *l*-tetrahydroquinaldine with a rotatory power in a 1-dcm. tube of α_D −50·38° (*Ber.*, 1894, **27**, 78), and, with the aid of *l*-tartaric acid, has recently obtained *d*-tetrahydroquinaldine with α_D +50·58° (Ladenburg and Herrmann, *Ber.*, 1908, **41**, 966). As we now show that the optically active tetrahydroquinaldines have a rotatory power of α_D 61·13° to 61·20° in 1-dcm. tubes, it appears that Ladenburg's purest specimens of the active bases contained about 5 per cent. of the enantiomorphously related isomerides.

Although the optically active bases could not be caused to crystallise, a mixture of equal weights of each crystallised readily when inoculated with a crystal of the racemic base.

d-(l-)*Tetrahydroquinaldine* d-(l-)*α-Bromocamphor-π-sulphonate.*

On dissolving pure *d*-tetrahydroquinaldine in the equivalent quantity of *d*-α-bromocamphor-π-sulphonic acid solution and evaporating to dryness, a gummy residue is obtained, which crystallises when rubbed in contact with dry ether. After crystallisation from ethyl acetate, the salt is obtained in small, colourless needles, melting at 162—165°. It is very soluble in water or alcohol, but less so in ethyl acetate. The salt which is enantiomorphously related to the foregoing is obtained in a similar manner, and it is noteworthy that the crystallisation of either salt is induced by inoculation with a crystal of the other:

0·0995, dried at 100°, gave 0·1903 CO_2 and 0·0548 H_2O. C=52·16; H=6·16.

$C_{20}H_{28}O_4NBrS$ requires C=52·37; H=6·16 per cent.

The salts behave similarly to their two isomerides in alcoholic solution, and exhibit mutarotation, which could not be accurately determined owing to the gradual darkening of the solutions on preservation; the observed specific rotatory powers varied between $[\alpha]_D$ 96° and 101°, $[\alpha]_{Hg\ (yellow)}$ 101° and 107°, and $[\alpha]_{Hg\ (green)}$ 118° and 124° in 1 per cent. solutions.

The following determinations were made in aqueous solutions at 17° in 4-dcm. tubes:

	d-*Base*, d-*Acid*.			l-*Base*, l-*Acid*.		
	0·2143 gram in 30 c.c.			0·2082 gram in 30 c.c.		
	Na(*D* line).	Hg(yellow).	Hg(green).	Na(*D* line).	Hg(yellow).	Hg(green).
α	+2·50°	+2·61°	+3·05°	−2·42°	−2·54°	2·96°
[α]	+87·49	+91·34	+106·74	−87·18	−91·50	−106 63

Mean values: $[M]_D$ 400·2°; $[M]_{Hg\ (yellow)}$ 419·0°; $[M]_{Hg\ (green)}$ 488 9°.

The mean rotatory dispersions in aqueous solution are, for $Hg_{(green)}/Na_{(yellow)}$ = 1·222, and for $Hg_{(yellow)}/Na_{(yellow)}$ = 1·047.

d- *and* l-*Tetrahydroquinaldine Hydrochloride*, $C_{10}H_{13}N,HCl,H_2O$.

For comparison with the salts with optically active acids, it seemed desirable to determine the rotatory powers of the hydrochlorides prepared from pure *d*- and *l*-tetrahydroquinaldine; these salts were prepared as already described, and recrystallised from acetone. The following determinations were made in aqueous solution in 4-dcm. tubes at 17°:

Hydrochloride of d-*Base.*

Weight in 30 c.c.		Na(*D* line).	Hg(yellow).	Hg(green).
0·1111 gram	α	+ 0·99°	+ 1·02°	+ 1·17°
	[α]	66·83	68·86	78·98
0·2004 ,,	α	1 78	1·84	2·10
	[α]	66·62	68·86	78·59
0·4116 ,,	α	3·64	3·78	4·31
	[α]	66·33	68·88	78·53

Hydrochloride of l*-Base.*

Weight in 30 c.c.		$\mathrm{Na}_{(D\ \mathrm{line})}$.	$\mathrm{Hg}_{(\mathrm{yellow})}$.	$\mathrm{Hg}_{(\mathrm{green})}$.
0·1136 gram	α	−1·01°	−1·05°	−1·20°
	$[\alpha]$	66·68	69·32	79·23
0·2062 ,,	α	1·83	1·90	2·18
	$[\alpha]$	66·56	69·11	79·29
0·4017 ,,	α	3·56	3·70	4·23
	$[\alpha]$	66·47	69·80	78·98

Mean molecular rotatory powers: $[M]_D$ 134·24°; $[M]_{\mathrm{Hg\ (yellow)}}$ 139·15°; $[M]_{\mathrm{Hg\ (green)}}$ 159·14°.

The mean rotatory dispersions are, for $\mathrm{Hg}_{(\mathrm{green})}/\mathrm{Na}_{(\mathrm{yellow})} = 1{\cdot}186$, and for $\mathrm{Hg}_{(\mathrm{yellow})}/\mathrm{Na}_{(\mathrm{yellow})} = 1{\cdot}037$.

It will be seen that the values for the two hydrochlorides agree very closely, and that the specific rotatory power decreases slowly as the concentration increases. The mean values are appreciably higher than were obtained by Pope and Peachey, who found the value $[M]_D$ −121·7° for *l*-tetrahydroquinaldine hydrochloride in dilute aqueous solution.

From the values now recorded, the molecular rotatory powers of the optically active basic and acidic ions can be calculated for comparison with those directly observed with the tetrahydroquinaldine hydrochlorides and the ammonium α-bromocamphor-π-sulphonates by means of the formulæ:

$$[M] \text{ of } d\mathrm{B}d\mathrm{A} + [M] \text{ of } l\mathrm{B}d\mathrm{A} = \text{Twice } [M] \text{ of } d\mathrm{A} \text{ ion.}$$
$$[M] \text{ of } d\mathrm{B}d\mathrm{A} - [M] \text{ of } l\mathrm{B}d\mathrm{A} = \text{Twice } [M] \text{ of } d\mathrm{B} \text{ ion.}$$

The following values are thus calculated:

	Basic ion.			*Acidic ion.*		
	$\mathrm{Na}_{(D\ \mathrm{line})}$.	$\mathrm{Hg}_{(\mathrm{yellow})}$.	$\mathrm{Hg}_{(\mathrm{green})}$.	$\mathrm{Na}_{(D\ \mathrm{line})}$.	$\mathrm{Hg}_{(\mathrm{yellow})}$.	$\mathrm{Hg}_{(\mathrm{green})}$.
[M]	126·4°	131·7°	152·2°	273·8°	287·3°	337·8°

Dispersions: $\mathrm{Hg}_{(\mathrm{green})}/\mathrm{Na}_{(\mathrm{yellow})} = 1{\cdot}203$; $\mathrm{Hg}_{(\mathrm{green})}/\mathrm{Na}_{(\mathrm{yellow})} = 1{\cdot}230$;
$\mathrm{Hg}_{(\mathrm{yellow})}/\mathrm{Na}_{(\mathrm{yellow})} = 1{\cdot}041$; $\mathrm{Hg}_{(\mathrm{yellow})}/\mathrm{Na}_{(\mathrm{yellow})} = 1{\cdot}049$.

The appended values are those deduced from the examination of the hydrochlorides of the base and the ammonium salts of the optically active acids:

	$\mathrm{Na}_{(D\ \mathrm{line})}$.	$\mathrm{Hg}_{(\mathrm{yellow})}$.	$\mathrm{Hg}_{(\mathrm{green})}$.	$\mathrm{Na}_{(D\ \mathrm{line})}$.	$\mathrm{Hg}_{(\mathrm{yellow})}$.	$\mathrm{Hg}_{(\mathrm{green})}$.
[M]	134·2°	139·1°	159·1°	278·7°	295·2°	346·6°

Dispersions: $\mathrm{Hg}_{(\mathrm{green})}/\mathrm{Na}_{(\mathrm{yellow})} = 1{\cdot}186$; $\mathrm{Hg}_{(\mathrm{green})}/\mathrm{Na}_{(\mathrm{yellow})} = 1{\cdot}243$;
$\mathrm{Hg}_{(\mathrm{yellow})}/\mathrm{Na}_{(\mathrm{yellow})} = 1{\cdot}037$; $\mathrm{Hg}_{(\mathrm{yellow})}/\mathrm{Na}_{(\mathrm{yellow})} = 1{\cdot}059$.

It is noteworthy that, although the molecular rotatory powers and dispersions calculated in the two different ways respectively are of the same order, the differences are much greater than could be attributed to experimental error. The discrepancies are scarcely traceable to the disregard of the concentration of the solutions examined, and are possibly due to the operation of isomeric change (compare Kipping, Trans., 1905, **87**, 628); the whole question is now being further studied.

The Optically Active Benzoyltetrahydroquinaldines.

With the aid of the pure optically active tetrahydroquinaldines which have been now prepared, it is possible to obtain the benzoyl derivatives in a greater state of purity than previously, and to make standard measurements of their rotation constants; these are of interest because the sign of rotation of the base changes during preparation of the benzoyl derivative. The benzoyl derivatives were prepared in the manner already described, and the following determinations made in absolute alcoholic solution in 4-dcm. tubes:

Benzoyl-d-*tetrahydroquinaldine.*

Weight in 30 c.c.	*t.*		Na(*D* line).	Hg(yellow).	Hg(green).
0·1602 gram	17°	α	− 7·03°	− 7·40°	− 8·59°
		$[\alpha]$	329·1	346·4	402·1
0·5031 gram	18	α	21·93	23·00	26·68
		$[\alpha]$	326·9	342·9	397·7

Benzoyl-l-*tetrahydroquinaldine.*

Weight in 30 c.c.	*t.*		Na(*D* line).	Hg(yellow).	Hg(green).
0·1751 gram	17°	α	+ 7·70°	+ 8·08°	+ 9·40°
		$[\alpha]$	329·8	346·1	402·6
0·5067 gram	18	α	22·07	23·12	26·84
		$[\alpha]$	326·7	342·2	397·3

The agreement between the specific rotatory powers of the *d*- and *l*-isomerides for similar concentration and identical wave-length is very close. The mean specific rotatory powers are, for the lower concentration at 17°:

$$[\alpha]_D\ 329{\cdot}46^\circ;\ [\alpha]_{Hg\,(yellow)}\ 346{\cdot}26^\circ;\ [\alpha]_{Hg\,(green)}\ 402{\cdot}38^\circ.$$

The rotatory dispersions are, for $Hg_{(green)}/Na_{(yellow)} = 1{\cdot}221$, and for $Hg_{(yellow)}/Na_{(yellow)} = 1{\cdot}051$.

For the higher concentration at 18°, the mean values are:

$$[\alpha]_D\ 326{\cdot}79^\circ;\ [\alpha]_{Hg\,(yellow)}\ 342{\cdot}54^\circ;\ [\alpha]_{Hg\,(green)}\ 397{\cdot}50^\circ.$$

The rotatory dispersions are, for $Hg_{(green)}/Na_{(yellow)} = 1{\cdot}217$, and for $Hg_{(yellow)}/Na_{(yellow)} = 1{\cdot}048$.

In view of the obvious high order of accuracy of the above determinations, it can be safely concluded that the rotatory dispersions of the benzoyl derivatives diminish slightly as the concentration increases, and that the rotatory dispersions of the benzoyl derivatives and those of the parent bases are not identical.

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CCXXIX.—*The Resolution of Externally Compensated Pavine and α-Bromocamphor-π-sulphonic Acid.*

By WILLIAM JACKSON POPE and CHARLES STANLEY GIBSON.

PYMAN has recently demonstrated the probability (Trans., 1909, **95**, 1610) that the "tetrahydropapaverine" described by Goldschmiedt (*Monatsh.*, 1886, **7**, 485; 1898, **19**, 324) is the 1:2-dihydropapaverine; some little uncertainty still remains as to the constitution of Goldschmiedt's base, and Pyman and Reynolds (this vol., p. 1320) consequently prefer to call the substance pavine. The presence of an asymmetric carbon atom in the molecule of "tetrahydropapaverine," or pavine, was demonstrated by the resolution of the base into its optically active components (Pope and Peachey, Trans., 1898, **73**, 893), but in view of the interest which now attaches to pavine it seemed desirable to apply to its resolution the methods which have been developed since that date.

Preparation of Externally Compensated Pavine.

The method of reducing papaverine described by Pyman yields the true tetrahydropapaverine as the chief product; the following process furnishes good yields of pavine. Papaverine (35 grams), hydrochloric acid (480 c.c.), and water (800 c.c.) are heated together under reflux, powdered tin (95 grams) being added in small portions; the tin becomes completely dissolved after about twenty hours' boiling, and, on cooling, a white, crystalline double salt separates. The latter is crystallised once from boiling water, and freed from tin by precipitation with hydrogen sulphide in boiling aqueous solution; the filtered solution, on evaporation, yields pavine hydrochloride, which is purified by crystallisation from hot water. About one-quarter of the papaverine used is thus obtained as pavine, whilst the mother liquors contain both the latter base and tetrahydropapaverine. This considerable yield of pavine is of interest in connexion with the suggestion, made and rejected by Pyman and Reynolds (*loc. cit.*), that this base is formed from some impurity present in the papaverine used.

Resolution of Externally Compensated Pavine.

The resolution of pavine into its optically active components, by crystallising the externally compensated base with one equivalent of *d*-bromocamphor-π-sulphonic acid, as described by Pope and Peachey, proceeds slowly, because the sparingly soluble crystalline salt of the lævo-component and the resinous salt of the dextro-component separate together; the former salt is with difficulty purified from the latter by crystallisation. The following application of Pope and Peachey's method (Trans., 1899, **75**, 1066) leads to a more satisfactory resolution of the base into its optically active components.

Externally compensated pavine hydrochloride is treated with one-half an equivalent proportion of ammonium *d*-α-bromocamphor-π-sulphonate in hot aqueous solution; on cooling, *l*-pavine *d*-α-bromocamphor-π-sulphonate separates in long needles not contaminated by the resinous salt of the *d*-base. That the salt *l*B*d*A thus obtained contained none of the salt *d*B*d*A was shown by treating it, without recrystallisation, with ammonia, and determining the specific rotatory power of the liberated base; in an 8 per cent. chloroform solution the value $[\alpha]_D$ $-152{\cdot}0°$ was obtained, which agrees well with the more accurately determined constant given below. It is clear that the resolution proceeds in accordance with the first type distinguished by Pope and Read (this vol., p. 989).

Although the separation of a pure *l*-pavine salt is rendered easy by the above method, yet the yield is not large, because on working in concentrated solutions, or on concentrating the mother liquors, hydrochloride of the base crystallises together with the salt *l*B*d*A; the following modification of the original process, which is applicable in other cases, was therefore adopted. The salts formed by pavine with inorganic acids are in general sparingly soluble in water, but Pope and Peachey found that the *d*-camphor-β-sulphonates of the base are readily soluble in water (Trans., 1898, **73**, 902); the externally compensated pavine was therefore dissolved in one equivalent proportion of *d*-camphor-β-sulphonic acid, and to the solution was added half an equivalent of ammonium *d*-α-bromocamphor-π-sulphonate, water being used as the solvent, and the solution being kept as concentrated as conveniently possible. Of the number of salts which might be formed in the mixed solution, *l*-pavine *d*-α-bromocamphor-π-sulphonate is the least soluble, and, as only sufficient ammonium salt was added to allow of the formation of this salt, it was to be expected that practically the whole of the *l*-pavine would separate as the pure salt. In accordance with this anticipation, the solution, prepared as described above, deposited almost all of the *l*-pavine as the sparingly soluble *d*-α-bromocamphor-π-sulphonate, and the deposited salt, after once recrystallising from boiling aqueous alcohol, has the properties previously ascribed to it.

After the *l*-pavine *d*-α-bromocamphor-π-sulphonate has been obtained in a pure state, the residual base—consisting almost entirely of *d*-pavine—is precipitated from the mother liquors by addition of ammonia, and its actual content of *d*-pavine determined from its rotatory power in chloroform solution; the base is then dissolved in the requisite amount of *d*-camphor-β-sulphonic acid solution, and ammonium *l*-α-bromocamphor-π-sulphonate added in just sufficient quantity to precipitate all the *d*-pavine as the salt *d*B*l*A, which, being enantiomorphously related to the crystalline salt *l*B*d*A dealt with above, exhibits ordinary physical properties identical with those of the latter.

d-*Pavine* l-*α-Bromocamphor-π-sulphonate*, $C_{20}H_{23}O_4N,C_{10}H_{14}OBr\cdot SO_3H$.

This new salt separates immediately in long, colourless needles when the above operation is performed; after cooling, the salt is collected and recrystallised from boiling aqueous alcohol. The substance decomposes at 290—300°, and gave the following results on analysis:

0·0933 gave 0·1888 CO_2 and 0·0482 H_2O. C=55·19; H=5·78.

$C_{30}H_{38}O_8NBrS$ requires C=55·19; H=5·87 per cent.

d- *and* l-*Pavine*.

These substances separate on cooling a hot dilute alcoholic solution of the corresponding bromocamphorsulphonates after addition of ammonia; after recrystallisation from benzene, the bases melted at 224°. The following determinations of rotatory power were made with the recrystallised substances after drying at 110°:

l-*Pavine*.

0·1983 gram, made up to 20 c.c. with chloroform, in a 2-dcm. tube at 23°:

	Na(*D* line).	Hg(yellow).	Hg(green).
α	−2·990°	−3·119°	−3·500°
$[\alpha]$	−150·8	−157·3	−176·5

0·7316 gram, made up to 20 c.c. with chloroform, in a 1-dcm. tube at 22°:

	Na(*D* line).	Hg(yellow).	Hg(green).
α	−5·445°	−5·730°	−6·500°
$[\alpha]$	−148·8	−156·6	−177·7

d-*Pavine*.

0·1970 gram, made up to 20 c.c. with chloroform, in a 2-dcm. tube at 23°:

	Na(*D* line).	Hg(yellow).	Hg(green).
α	+2·960°	+3·093°	+3·470°
$[\alpha]$	+150·3	+157·0	+176·1

0·7033 gram, made up to 20 c.c. with chloroform, in a 1 dcm. tube at 22°:

	Na(*D* line).	Hg(yellow).	Hg(green).
α	+5·241°	+5·520°	+6·250°
$[\alpha]$	+149·0	+157·0	+177·7

The values obtained under similar conditions for the two enantiomorphously related bases are in good agreement, and are slightly higher than those previously recorded; the specific rotatory power diminishes slowly with increasing concentration, and the numbers afford some indication that the rotatory dispersion is dependent on the concentration of the solution.

dl-*Pavine* dl-*α-Bromocamphor-π-sulphonate*, $2C_{20}H_{23}O_4N,2C_{10}H_{14}OBr\cdot SO_3H,H_2O$.

In view of the sparing solubility of the two crystalline salts dealt with above, namely, *l*B*d*A and *d*B*l*A, and of the fact that the salts *d*B*d*A and *l*B*l*A are resinous and also sparingly soluble, it seemed desirable to examine the salt formed by externally compensated pavine with the externally compensated α-bromocamphor-π-sulphonic acid. This substance was easily prepared by dissolving *dl*-pavine in an aqueous solution of the requisite amount of *dl*-α-bromocamphor-π-sulphonic acid, and evaporating to a gummy consistency; the residue crystallises on keeping, and after several recrystallisations from strong alcohol the salt is obtained in radiate clusters of soft, white, silky needles. The salt is optically inactive in aqueous solution, and the following analyses were made on the air-dried material:

0·1111 gave 0·2204 CO_2 and 0·0595 H_2O. C=54·11; H=5·97.

0·3233, heated at 110° for three hours, lost 0·0044. H_2O=1·36.

$C_{60}H_{76}O_{16}N_2Br_2S_2,H_2O$ requires C=54·44; H=5·94; H_2O=1·36 per cent.

This fully racemic salt thus differs from the active ones previously described, which crystallise without water, in containing water of crystallisation; it is also very soluble in water, and melts without blackening at 248—250°, whilst the active salts are sparingly soluble and decompose at 290—300°.

The Resolution of Externally Compensated α-Bromocamphor-π-sulphonic Acid.

The ease with which the resolution of externally compensated pavine can be effected with the aid of *d*- and *l*-α-bromocamphor-π-sulphonic acid suggests that the optically active bases could be used in effecting the resolution of the externally compensated acid in accordance with the method of Pope and Peachey.

With this object, an aqueous solution was prepared containing *d*-pavine (one equivalent), ammonia (one equivalent), and *dl*-α-bromocamphor-π-sulphonic acid; a clear solution is obtained on boiling with addition of a little alcohol, and, on cooling, the greater part of the alkaloid separates as the crystalline *d*-pavine *l*-α-bromocamphor-π-sulphonate. After recrystallisation from water, the latter salt was treated with ammonia, and the resulting ammonium *l*-α-bromocamphor-π-sulphonate separated by crystallisation; 0·1080 gram of this ammonium salt, made up to 20 c.c. with water, gave α_D −0·915° in a 2-dcm. tube at 22°, whence $[\alpha]_D$ −84·7°. The latter value is identical with that observed with ammonium *l*-α-bromocamphor-π-sulphonate prepared from *l*-camphor, so that the resolution of the externally compensated acid has been effected.

The mother liquors from which the *d*-pavine salt had been separated were next treated with ammonia, filtered, and evaporated until crystallisation occurred; on recrystallising the residue from aqueous alcohol, pure ammonium *d*-α-bromocamphor-π-sulphonate was obtained. 0·1082 gram, made up to 20 c.c. with water, gave α_D +0·915° in a 2-dcm. tube at 22°, whence $[\alpha]_D$ +84·6°, which is the value ordinarily assigned to pure ammonium *d*-α-bromocamphor-π-sulphonate.

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CCXXX.—*The Rotatory Powers of the Salts of* d- *and* l-*Camphor-β-sulphonic Acid with* d- *and* l-*Pavine.*

By **WILLIAM JACKSON POPE** and **CHARLES STANLEY GIBSON.**

IT has been repeatedly shown that a knowledge of molecular rotatory power in aqueous solution renders great service in connexion with the resolution of externally compensated bases (or acids) by crystallisation with a powerful optically active acid (or base); the theoretical scheme which leads to the indicated use of rotatory power determinations is too well known to require recapitulation (see preceding paper). At the same time, the experimental data on which the scheme is based are not very extensive, and it is of importance to collect further evidence in justification of the extended use now so frequently made of determinations of molecular rotatory powers in aqueous solutions. For this reason, we have made a careful polarimetric examination of the *d*- and *l*-pavine *d*- and *l*-camphor-β-sulphonates, and have appended thereto a description of a number of metallic salts of the latter acids.

d-*Pavine* d-*Camphor-β-sulphonate and* l-*Pavine* l-*Camphor-β-sulphonate*, $C_{20}H_{23}O_4N,C_{10}H_{15}O\cdot SO_3H$.

These salts are obtained by boiling equivalent quantities of the silver salt of the corresponding acid with the hydrochloride of the corresponding base in aqueous solution; after filtration and concentration, they are obtained crystalline, and, on recrystallisation from hot alcohol, separate in glistening clusters of colourless, transparent prisms. They are very soluble in water or hot alcohol, less so in acetone or cold alcohol, and almost insoluble in benzene or ether, and do not melt on heating:

0·1156 of *d*-salt gave 0·2656 CO_2 and 0·0708 H_2O. C = 62·67; H = 6·85.

0·1175 of *l*-salt gave 0·2694 CO_2 and 0·0726 H_2O. C = 62·39; H = 6·93.

$C_{30}H_{39}O_8NS$ requires C = 62·78; H = 6·86 per cent.

The following determinations of rotatory power were made in 2-dcm. tubes at 21°, water being used as the solvent:

	*d*B*d*A.			*l*B*l*A.		
	0·1094 gram in 20 c.c.			0·1142 gram in 20 c.c.		
	Na(*D* line).	Hg(yellow).	Hg(green).	Na(*D* line).	Hg(yellow).	Hg(green).
α	+1·372°	+1·454°	+1·663°	−1·438°	−1·510°	−1·733°
[α]	+125·4	+132·9	+152·0	−125·9	−132·2	−151·7
[M]	+718·7	+761·5	+871·0	−721·5	−757·5	−869·3

From the above values the mean molecular rotatory powers of the salts *d*B*d*A and *l*B*l*A in dilute aqueous solution are calculated as $[M]_D \pm 720·1°$, $[M]_{Hg\ (yel.)} \pm 759·5°$, and $[M]_{Hg\ (green)} \pm 870·1°$. The molecular rotatory dispersions are for $Hg_{(green)}/Na_{(yellow)} = 1·208$, and for $Hg_{(yellow)}/Na_{(yellow)} = 1·055$.

d-*Pavine* l-*Camphor-β-sulphonate and* l-*Pavine* d-*Camphor-β-sulphonate, d*B*l*A *and l*B*d*A.

These salts were prepared and crystallised in the same way as the two preceding ones, from which they differ but little in solubilities and general physical properties; they crystallise in small, colourless needles:

0·1189 *d*B*l*A gave 0·2726 CO_2 and 0·0716 H_2O. C = 62·53; H = 6·74.
0·1033 *l*B*d*A „ 0·2370 CO_2 „ 0·0645 H_2O. C = 62·57; H = 6·98.

$C_{30}H_{39}O_8NS$ requires C = 62·78; H = 6·86 per cent.

The following determinations of rotatory power were made in 2-dcm. tubes at 20°, water being the solvent:

	*d*B*l*A.			*l*B*d*A.		
	0·1200 gram in 20 c.c.			0·1226 gram in 20 c.c.		
	Na (*D* line).	Hg (yellow).	Hg (green).	Na (*D* line).	Hg (yellow).	Hg (green).
α	+1·315°	+1·365°	+1·540°	−1·340°	−1·380°	−1·580°
[α]	+109·6	+113·8	+128·3	−109·3	−113·6	−128·9
[M]	+628·1	+652·1	+735·1	−626·3	−651·0	−738·6

The mean molecular rotatory dispersions of the salts *d*B*l*A and *l*B*d*A in dilute aqueous solution are hence calculated as:

$$[M]_D \pm 627·2°,\ [M]_{Hg\ (yel.)} \pm 651·5°,\ \text{and}\ [M]_{Hg\ (green)} \pm 736·8°.$$

The molecular rotatory dispersions are for Hg$_{(green)}$/Na$_{(yellow)}$ = 1·175, and for Hg$_{(yellow)}$/Na$_{(yellow)}$ = 1·039; these values differ considerably from the corresponding rotatory dispersions for the salts *d*B*d*A and *l*B*l*A, and this, as will be shown below, is to be traced to the differences in molecular rotatory dispersion between the basic and the acid ions.

It has been shown by Pope and Peachey (Trans., 1899, **75**, 1084) that the molecular rotatory powers of the basic and acidic ions may be calculated in the following manner from the molecular rotatory powers of the salts *d*B*d*A and *d*B*l*A in dilute aqueous solutions:

[M] of *d*B*d*A + [M] of *d*B*l*A = Twice [M] of *d*B ion.
[M] of *d*B*d*A − [M] of *d*B*l*A = Twice [M] of *d*A ion.

Applying these formulæ to the values given above, the following are obtained:

	Molecular rotations.			Rotatory dispersions.	
	Na (*D* line).	Hg (yellow).	Hg (green).	Hg (green)/ Na(yellow).	Hg(yellow)/ Na(yellow).
d-Base ion	+673·6°	+705·5°	+803·4°	1·193	1·047
d-Acid ion	+46·4	+54·0	+66·6	1·435	1·163

Consideration of the above table indicates that the discrepancies between the rotatory dispersions of the two pairs of enantiomorphously related salts are due to the existence of considerable differences between the rotatory dispersions of the basic and acidic ions produced from the salts in aqueous solution. Whilst the optical behaviour of the salts in question is up to this point entirely in accordance with what would be expected, it is at least remarkable that the molecular rotatory power of the acidic ion is considerably smaller than the value hitherto accepted; the examination of the ammonium salt of *d*-camphor-β-sulphonic acid and of the salts which the latter forms with *d*- and *l*-tetrahydroquinaldine (Pope and Peachey, Trans., 1899, **75**, 1085) leads to the conclusion that the acidic ion has the molecular rotatory power $[M]_D$ +51·7°, whilst the results stated above indicate that the value should be taken as $[M]_D$ +46·4° It thus seemed important to obtain further experimental data to supplement the small amount of information now available concerning the rotatory powers of the *d*-camphor-β-sulphonates, and Mr. P. V. Delahunty, M.Sc.Tech., has examined carefully purified samples of a number of such salts and of the parent acid; the results of his determinations are now given.

d-*Camphor-β-sulphonic Acid.*

This acid was prepared by the method described by Reychler (*Bull Soc. chim.*, 1898, [iii], **19**, 120), and, after separation from the acetic acid solution, was recrystallised repeatedly from ethyl acetate; during the crystallisation it was several times exposed over alkali hydroxide in a vacuum to free it from acetic acid, which it retains with some tenacity. Solutions of the purified acid dissolve magnesium freely in the cold and zinc on slight warming, but do not act on copper at the boiling point; the crystalline acid was subsequently exposed to the air, and the following determinations made with two separate preparations:

1·0012 required 0·15624 Na·OH for neutralisation.
$C_{10}H_{15}O \cdot SO_3H = 90·51$.
2·1170 required 0·33006 Na·OH for neutralisation.
$C_{10}H_{15}O \cdot SO_3H = 90·41$.
$2C_{10}H_{15}O \cdot SO_3H,3H_2O$ requires $C_{10}H_{15}O \cdot SO_3H = 89·58$.

The above sample of the acid, which thus contains 90·45 per cent. of camphorsulphonic acid, gave the following results on determination of rotatory power in aqueous solution in 2-dcm. tubes at 16°:

Weight in 25 c.c.		a_D.	$[a]_D$.	$[M]_D$.
1·1713 grams	......	+1·82°	+21·44°	+49·7°
1·0430 ,,	......	+1·65	+21·86	+50·7
1·0431 ,,	......	+1·63	+21·59	+50·1

The mean molecular rotatory power in the dilute aqueous solution is thus $[M]_D$ +50·2°.

Ammonium d-*Camphor-β-sulphonate.*

This salt was prepared in the usual manner, and was obtained as a mass of white needles; three separate preparations indicated, on distillation with soda and titration with acid, the presence of 7·59, 7·69, and 7·64 per cent. of ammonium, NH_4, respectively, in place of the theoretical percentage of 7·23. The cause of this slight discrepancy was not traced. The following determinations were made in aqueous solutions at 16°, 2-dcm. tubes being used:

Grams in 25 c.c.	a_D.	$[a]_D$.	$[M]_D$.
1·1726	+1·92°	+20·46°	+50·9°
1·0536	1·72	20·40	50·8
1·1295	1·85	20·47	50·8

The mean molecular rotatory power in dilute aqueous solution is thus $[M]_D$ +50·8°.

Potassium d-*Camphor-β-sulphonate.*

This salt was prepared in the usual manner, and when purified by crystallisation from alcohol, is obtained in colourless needles, which contain no solvent of crystallisation:

0·7860 gave 0·7150 K_2PtCl_6. K = 14·60.

$C_{10}H_{15}O_4SK$ requires K = 14·44 per cent.

The following determinations of rotatory power were made in aqueous solutions at 16° in 2-dcm. tubes:

Grams in 25 c.c.	α_D.	$[\alpha]_D$.	$[M]_D$.
1·1190	+1·64°	+18·32°	+49·5°
1·0956	1·61	18·37	49·6
1·0910	1·60	18·33	49·5

Calcium d-*Camphor-β-sulphonate.*

On treating a solution of the acid with lime, precipitating the excess of the latter with carbon dioxide, filtering, and concentrating, the calcium salt is obtained in large, colourless prisms:

1·0685 gave 0·2540 $CaSO_4$. Ca = 6·99.

2·0298 lost 0·2613 at 105°. H_2O = 12·87.

$(C_{10}H_{15}O_4S)_2Ca,4H_2O$ requires Ca = 6·97; H_2O = 12·54 per cent.

The following determinations were made in aqueous solutions at 16° in 2-dcm. tubes:

Grams in 25 c.c.	α_D.	$[\alpha]_D$.	$[M]_D$.
1·0042	+1·39°	+17·30°	+49·6°
1·0184	1·40	17·18	49·3
1·2048	1·65	17·12	49·1

The mean molecular rotatory power in dilute aqueous solution is thus $[M]_D$ +49·3°.

Barium d-*Camphor-β-sulphonate*, $(C_{10}H_{15}O\cdot SO_3)_2Ba,3H_2O$.

This salt was prepared by treating the ammonium salt with baryta, separating the excess of the latter in the usual way, and concentrating the filtered solution until crystallisation occurred; it was purified by recrystallisation from water, and finally obtained in colourless needles. The solvent of crystallisation is only lost completely at 120—130°, and the anhydrous salt is hygroscopic:

1·0124 gave 0·3600 $BaSO_4$. Ba = 20·90.

1·7860 lost 0·1473 at 130°. H_2O = 8·25.

$(C_{10}H_{15}O_4S)_2Ba,3H_2O$ requires Ba = 20·98; H_2O = 8·27 per cent.

The following determinations were made in aqueous solutions at 16° in 2-dcm. tubes:

Grams in 25 c.c.	α_D.	$[\alpha]_D$.	$[M]_D$.
1·1760	+1·43°	+15·30°	+49·6°
1 0136	1·23	15·16	49·5
1·0422	1·27	15·23	49·7

The mean molecular rotatory power in dilute aqueous solution is thus $[M]_D$ +49·6°.

Zinc d-*Camphor-β-sulphonate,* $(C_{10}H_{15}O_4S)_2Zn,6H_2O$.

The zinc salt, prepared by double decomposition between the barium salt and zinc sulphate, crystallises in lustrous, six-sided prisms, which melt at 167°:

0·9052 lost 0·1540 at 130°. $H_2O=17·01$.

1·0136 gave 0·1300 ZnO. $Zn=10·29$.

$(C_{10}H_{15}O_4S)_2Zn,6H_2O$ requires $H_2O=17·01$; $Zn=10·33$ per cent.

The following determinations were made in aqueous solutions at 16° in 2-dcm. tubes:

Grams in 25 c.c.	α_D.	$[\alpha]_D$	$[M]_D$.
1·0001	+1·24°	+15·49°	+49·2°
1·0130	1·26	15·55	49·4
1·0132	1·25	15·42	49·0

The mean molecular rotatory power in aqueous solution is thus $[M]_D$ +49·2°.

Silver d-*Camphor-β-sulphonate,* $C_{10}H_{15}O{\cdot}SO_3Ag$.

This salt, prepared by dissolving silver hydroxide in the aqueous acid, crystallises in colourless needles, and is readily soluble in water and alcohol:

1·0506 gave 0·4466 AgCl. $Ag=31·97$.

$C_{10}H_{15}O_4SAg$ requires $Ag=31·86$ per cent.

The following determinations were made in aqueous solutions at 16° in 2-dcm. tubes:

Grams in 25 c.c.	α_D.	$[\alpha]_D$.	$[M]_D$.
1·0010	+1·17°	+14·61°	+49·5°
1·0730	1·25	14 56	49·4
1·1008	1·28	14·54	49·2

The mean molecular rotatory power in dilute aqueous solution is thus $[M]_D$ +49·4°.

In addition to the salts described above, the cupric salt, crystallising with 5·5 molecules of water in pale blue rhombs, and the ferric salt, crystallising in yellowish-green leaflets, have also been prepared.

It is noteworthy that in the concentrations used, all the above compounds, with the exception of the free acid and its ammonium salt, give molecular rotatory powers less than $[M]_D$ +50°; this value is notably less than was obtained by Pope and Peachey from examination of the ammonium salt. The still smaller value of $[M]_D$ +46·4° obtained for the acidic ion by the examination of the pavine salts described above possibly result from the greater degree of molecular dilution in which the latter salts were examined; in this connexion, it is worthy of note that Walden (*Zeitsch. physikal. Chem.*, 1894, **15**, 196) found that the molecular rotatory powers of the *d*-α-bromocamphor-π-sulphonates decreased slightly as the dilution increased in aqueous solution.

d- *and* l-*Pavine* d-*Tartrates.*

Since externally compensated pavine cannot be resolved by crystallisation with *d*-tartaric acid, owing to the formation of a well-characterised partly racemic *dl*-pavine *d*-tartrate (Goldschmiedt, *Monatsh.*, 1898, **19**, 321; Pope and Peachey, Trans., 1898, **73**, 902), it appeared of interest to prepare and examine the *d*-tartrates of both *d*- and *l*-pavine. The salts were prepared by dissolving equivalent quantities of the base and acid in aqueous alcohol and evaporating to dryness; the partly crystalline residues were then dissolved in dry acetone and precipitated as microcrystalline, white powders by the gradual addition of dry ether. Both salts absorb moisture from the air, and are extremely soluble in water and most organic solvents; they thus contrast strongly with *dl*-pavine *d*-tartrate, which is stable in the air, and dissolves sparingly in water and alcohol.

d-*Pavine* d-*Tartrate*, $2C_{20}H_{23}O_4N,C_4H_6O_6,6H_2O$.

This salt readily absorbs moisture after drying in a vacuum desiccator, and, for purposes of analysis, was exposed to the air until constant in weight:

0·1170 gave 0·2401 CO_2 and 0·0682 H_2O. $C=55·97$; $H=6·52$.
0·4364 lost 0·0394 at 105°. $H_2O=9·03$.
$C_{44}H_{64}O_{20}N_2$ requires $C=56·14$; $H=6·86$; $H_2O=11·50$ per cent.

An accurate determination of the water of crystallisation could not be made, because decomposition sets in before the salt becomes anhydrous; the above analyses merely show that the salt is the normal tartrate. It melts and decomposes at 156—158°:

0·2260 gram, dried at 105°, and made up to 20·0 c.c. with water at 22°, gave α_D +3·56° in a 2-dcm. tube, whence $[\alpha]_D$ +157·5°.

l-*Pavine* d-*Tartrate*, $2C_{20}H_{23}O_4N_2,C_4H_6O_6,H_2O$.

After drying at 105°, this salt was found by the following analyses to retain one molecule of water of crystallisation; like the corresponding salt of *d*-pavine, it melts and decomposes at 156—158°:

0·1658 gave 0·3759 CO_2 and 0·0950 H_2O. C = 61·81; H = 6·40.
0·1694 „ 0·3862 CO_2 „ 0·0968 H_2O. C = 62·16; H = 6·39.
$C_{44}H_{54}O_{15}N_2$ requires C = 62·10; H = 6·40 per cent.

0·2810 gram, made up to 20·0 c.c. with water at 22°, gave α_D −4·23° in a 2-dcm. tube, whence $[\alpha]_D$ −150·5°.

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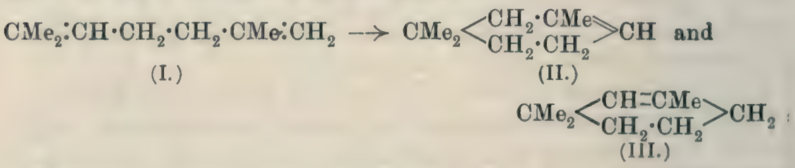
CAMBRIDGE.

CCXXXI.—*Synthesis of* 1 : 1 : 3-*Trimethyl*cyclo*hexene* (cyclo*Geraniolene*).

By ARTHUR WILLIAM CROSSLEY and CHARLES GILLING (Salters' Fellow).

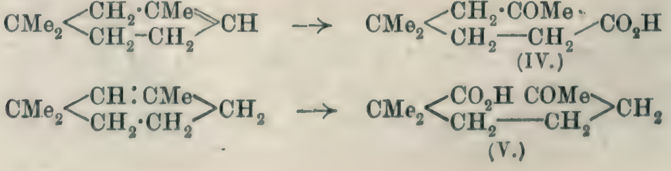
SOME years ago Tiemann and Semmler (*Ber.*, 1893, **26**, 2708) prepared from the aldehyde citral (geranial) an open-chain hydrocarbon, C_9H_{16}, named by them geraniolene. The constitution of this substance (I) follows from that of citral, which was established by Barbier and Bouveault in 1896 (*Compt. rend.*, **122**, 393).

When geraniolene is shaken with a 60 per cent. solution of sulphuric acid, an isomeric change takes place, the open-chain hydrocarbon being converted into a mixture of two cyclic hydrocarbons, α- and β-*cyclo*geraniolene (II and III), in which mixture the α-variety is present in larger quantity:



$$\underset{\text{(I.)}}{CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CH_2} \longrightarrow \underset{\text{(II.)}}{CMe_2\left<\begin{matrix}CH_2\cdot CMe\\CH_2\cdot CH_2\end{matrix}\right>CH} \text{ and } \underset{\text{(III.)}}{CMe_2\left<\begin{matrix}CH{:}CMe\\CH_2\cdot CH_2\end{matrix}\right>CH_2}$$

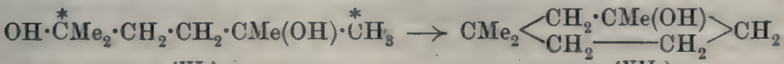
The constitutional formulæ of these hydrocarbons were ultimately determined by Tiemann (*Ber.*, 1898, **31**, 816, 881; 1900, **33**, 3711) from a study of their oxidation with potassium permanganate, the products isolated being two ketonic acids, *iso*geronic (IV) and geronic (V) acids, together with *as*-dimethylsuccinic acid and ββ-dimethylglutaric acid.



$$CMe_2\left<\begin{matrix}CH_2\cdot CMe\\CH_2-CH_2\end{matrix}\right>CH \longrightarrow \underset{\text{(IV.)}}{CMe_2\left<\begin{matrix}CH_2\cdot COMe\\CH_2-CH_2\end{matrix}\right>CO_2H}$$

$$CMe_2\left<\begin{matrix}CH{:}CMe\\CH_2\cdot CH_2\end{matrix}\right>CH_2 \longrightarrow \underset{\text{(V.)}}{CMe_2\left<\begin{matrix}CO_2H\ \ COMe\\CH_2-CH_2\end{matrix}\right>CH_2}$$

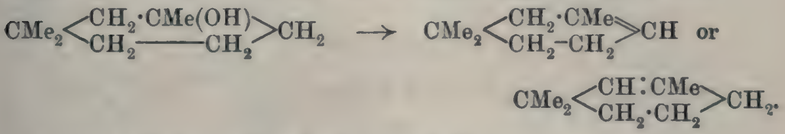
The formation of the two modifications of *cyclo*geraniolene was ascribed to the addition of two molecules of water to the molecule of geraniolene which were subsequently eliminated. According to Tiemann, hydroxyl groups became attached to the carbon atoms bearing methyl groups, so that the first stage in the reaction consists in the formation of a compound of formula VI; this is succeeded by ring-formation due to elimination of a molecule of water and subsequent union of the two carbon atoms marked *:



$$\mathrm{OH\cdot\overset{*}{C}Me_2\cdot CH_2\cdot CH_2\cdot CMe(OH)\cdot\overset{*}{C}H_3} \longrightarrow \mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot CMe(OH)}\\ \mathrm{CH_2{-\!-\!-}CH_2}\end{matrix}>\mathrm{CH_2}$$

(VI.) (VII.)

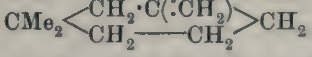
It is obvious that the second molecule of water may be eliminated from the compound (VII) in two different ways, and the formation of the two modifications of *cyclo*geraniolene is thus explained:



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot CMe(OH)}\\ \mathrm{CH_2{-\!-\!-}CH_2}\end{matrix}>\mathrm{CH_2} \longrightarrow \mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot CMe}\\ \mathrm{CH_2{-}CH_2}\end{matrix}>\mathrm{CH} \text{ or }$$

$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH\colon CMe}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH_2}.$$

A third hydrocarbon having the formula:

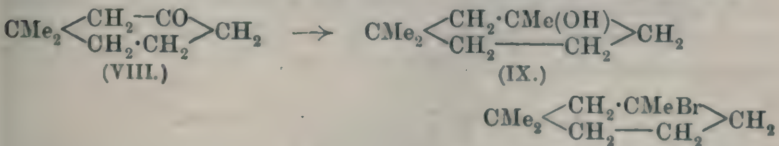


$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot C(\colon CH_2)}\\ \mathrm{CH_2{-\!-\!-}CH_2}\end{matrix}>\mathrm{CH_2}$$

is a possibility, but no evidence of its presence is recorded.

Tiemann did not actually isolate either of the hydroxy-compounds VI or VII, but a synthesis of 1 : 1 : 3-trimethyl*cyclo*hexan-3-ol (VII) has now been effected by a method which leaves no doubt as to its constitution, and it is found that this alcohol can be readily converted into *cyclo*geraniolene, thus affording confirmation of Tiemann's supposition.

The starting point was 1 : 1-dimethyl*cyclo*hexan-3-one (VIII), prepared by the action of reducing agents on 5-chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one (Trans., 1907, **91**, 81). When this ketone is treated with an ethereal solution of magnesium methyl iodide and the product decomposed with water, trimethyl*cyclo*hexanol (IX) is obtained as a well-defined, crystalline substance, melting at 72·5°



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2{-}CO}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH_2} \longrightarrow \mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot CMe(OH)}\\ \mathrm{CH_2{-\!-\!-}CH_2}\end{matrix}>\mathrm{CH_2}$$

(VIII.) (IX.)

$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot CMeBr}\\ \mathrm{CH_2{-\!-}CH_2}\end{matrix}>\mathrm{CH_2}$$

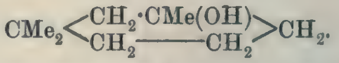
(X.)

Fuming hydrobromic acid converts the alcohol into 3-bromo-1 : 1 : 3-trimethyl*cyclo*hexane (X), which, when treated with alcoholic potassium hydroxide, loses the elements of hydrogen bromide in two ways, giving rise to the same mixture of hydrocarbons as described by Tiemann.

The work of Tiemann on the preparation of *cyclo*geraniolene was repeated by Wallach (*Annalen*, 1902, **324**, 97), who prepared the nitrosate of *a*-*cyclo*geraniolene, and proved that it was transformed by the action of alkalis into the oxime of 1 : 1 : 3-trimethyl-Δ^2-*cyclo*hexen-4-one. The identity of the hydrocarbons described in the present communication with *cyclo*geraniolene has been established by preparing this crystalline nitrosate, and from it the above-mentioned oxime; further, by oxidising the hydrocarbons with potassium permanganate, when the products isolated were *as*-dimethylsuccinic acid, *iso*geronic and geronic acids, the two latter being identified as their semicarbazones, melting at 195° and 164° respectively.

EXPERIMENTAL.

1 : 1 : 3-*Trimethyl*cyclo*hexan*-3-*ol*,



$$CMe_2<\begin{matrix}CH_2\cdot CMe(OH)\\ CH_2\text{———}CH_2\end{matrix}>CH_2.$$

Thirty grams of 1 : 1-dimethyl*cyclo*hexan-3-one (Trans., 1907, **91**, 81), dissolved in an equal volume of ether, were gradually added to a Grignard reagent prepared from 33 grams of methyl iodide and 5·7 grams of magnesium turnings in 100 c.c. of dry ether. The ethereal solution was gently boiled on a water-bath for one hour, cooled, and poured into a concentrated solution of ammonium chloride, to which ice had been added. The ethereal layer was separated, the saline solution extracted three times with ether, the mixed ethereal liquids washed, dried over potassium carbonate, and evaporated, when a solid residue (23 grams = 70 per cent. of the theoretical amount) was obtained, which, after drying on porous plate, was recrystallised from dilute alcohol and analysed:

0·1061 gave 0·2965 CO_2 and 0·1209 H_2O. C = 76·21; H = 12·66.

$C_9H_{18}O$ requires C = 76·06; H = 12·67 per cent.

1 : 1 : 3-*Trimethyl*cyclo*hexan*-3-*ol* is readily soluble in the cold in all the ordinary organic solvents, and may be crystallised from dilute alcohol or dilute acetone, from which it separates in beautiful four-sided, elongated prisms, having a characteristic, strongly camphoraceous odour, and melting at 72·5°.

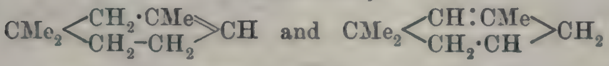
3-*Bromo*-1 : 1 : 3-*trimethyl*cyclo*hexane*.

Trimethyl*cyclo*hexanol, in quantities of 10 grams at one time, were sealed up with 50 c.c. of a solution of hydrogen bromide (saturated at 0°) in small soda-water bottles, which were heated in a boiling-water bath for one hour. The mixture was poured into water, extracted three times with ether, the ethereal solution washed with a solution of sodium hydrogen carbonate, then with water, dried, evaporated, and the residue distilled under diminished pressure, when, after two distillations, 11·5 grams passed over constantly at 88°/20 mm.:

0·1527 gave 0·1375 AgBr. Br = 38·31.
$C_9H_{17}Br$ requires Br = 39·02 per cent.

*Bromotrimethyl*cyclo*hexane* is, when freshly prepared, a faintly yellow liquid boiling at 88°/20 mm., which, especially on exposure to air, evolves fumes of hydrogen bromide and rapidly decomposes, becoming green, and finally black. The rapidity with which this decomposition takes place accounts, no doubt, for the low result for bromine quoted above.

1 : 1 : 3-*Trimethyl*-Δ^3- *and* -Δ^2-cyclo*hexenes.* α- *and* β-cyclo*Geraniolene,*



$CMe_2<\begin{matrix}CH_2\cdot CMe\\ CH_2-CH_2\end{matrix}>CH$ and $CMe_2<\begin{matrix}CH:CMe\\ CH_2\cdot CH\end{matrix}>CH_2$

Thirty grams of potassium hydroxide were dissolved in a little water, and added to 35 grams of bromotrimethyl*cyclo*hexane dissolved in 150 c.c. of absolute alcohol. The whole was heated on the water-bath for one hour, cooled, poured into water, and extracted four times with ether; the ethereal solution was washed, dried, and evaporated, and the residue distilled, when the following fractions were collected: 110—136° = 2 grams; 136—142° = 13 grams; 142—150° = 3 grams. The fraction 136—142° was twice redistilled over sodium and analysed:

0·1244 gave 0·3971 CO_2 and 0·1430 H_2O. C = 87·06; H = 12·77.
C_9H_{16} requires C = 87·10; H = 12·90 per cent.

*Trimethyl*cyclo*hexene* (cyclo*geraniolene*) is a colourless, refractive liquid, possessing a pronounced terpene-like odour. It boils at 137—140°/760 mm., and has a density of 0·8085 at 15°/15°.

This hydrocarbon has also been prepared by the action of dehydrating agents on trimethyl*cyclo*hexanol (potassium hydrogen sulphate at 130—140°, and zinc chloride at 160—170°) and by shaking trimethyl*cyclo*hexanol with dilute sulphuric acid (D 1·67) for several hours at the laboratory temperature. If this latter action is prolonged for several days, the principal product is a polymeric modification of the hydrocarbon boiling at 165—170°/30 mm.

When dissolved in glacial acetic acid and treated with amyl nitrite and nitric acid according to the directions of Wallach (*loc. cit.*), the mixture of trimethyl*cyclo*hexenes, prepared by any of these methods, yielded the crystalline nitrosate of 1 : 1 : 3-trimethyl-Δ^3-*cyclo*hexene, melting at 103—104°, which by the action of sodium methoxide was transformed into the oxime of 1 : 1 : 3-trimethyl-Δ^2-*cyclo*hexen-4-one, melting at 128°.

The hydrocarbon was oxidised with potassium permanganate as described by Tiemann (*Ber.*, 1900, **33**, 3711), when the residue obtained on working up the product partly solidified on keeping. It was spread on plate, and the residue crystallised from water, when it melted at 140°. The identity of this substance with *as*-dimethylsuccinic acid was proved by the mixed melting-point method, and by preparing from it an anilic acid, which melted at 186°.

The porous plate (see above), on extraction with ether, yielded an oil which was dissolved in alcohol and treated with a solution of semicarbazide acetate. After some time a solid was deposited, melting at 185—192°, which crystallised from alcohol, in which solvent it is only sparingly soluble, in feathery needles, melting and decomposing at 198°. (Found, N = 18·46. $C_{10}H_{19}O_3N_3$ requires N = 18·34 per cent.) These data prove the substance to be the semicarbazone of *iso*geronic acid.

On concentrating the mother liquor from the above semicarbazone, a further quantity of crystals was obtained in glistening lamellæ, melting, after recrystallisation, at 163°. (Found, N = 18·37. $C_{10}H_{19}O_3N_3$ requires N = 18·34 per cent.) The substance was therefore the semicarbazone of geronic acid (compare Tiemann).

It appeared to be of interest, in connexion with other work which is in hand, to try the action of Grignard reagents, other than magnesium methyl bromide, on dimethyl*cyclo*hexanone, but the results are most disappointing, as with increase in the molecular weight of the alkyl group, the yields of the products decrease rapidly, and further work in this direction has been abandoned for the present.

1 : 1-*Dimethyl-3-ethyl*cyclo*hexan-3-ol*, prepared by the action of magnesium ethyl bromide on 1 : 1-dimethyl*cyclo*hexan-3-one, is a colourless, refractive liquid, boiling at 94°/30 mm., and possessing a penetrating, camphoraceous odour:

0·1363 gave 0·3851 CO_2 and 0·1552 H_2O. C = 77·05; H = 12·65.

$C_{10}H_{20}O$ requires C = 76·93; H = 12·82 per cent.

The alcohol is readily converted by the action of fuming hydrobromic acid into 3-*bromo*-1 : 1-*dimethyl*-3-*ethyl*cyclo*hexane* (b. p. 105—106°/22 mm.), from which substance hydrogen bromide is eliminated by potassium hydroxide to give a mixture of isomeric 1 : 1-*dimethyl*-3-*ethyl*cyclo*hexenes*:

0·1210 gave 0·3848 CO_2 and 0·1425 H_2O. C = 86·73; H = 13·09.

$C_{10}H_{18}$ requires C = 86·95; H = 13·04 per cent.

*Dimethylethyl*cyclo*hexene* is a colourless, refractive liquid, boiling at 156°/760 mm.

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CCXXXII.—*The Constituents of Gelsemium.*

By Charles Watson Moore.

Under the title of "gelsemium" several of the pharmacopœias recognise the dried rhizome and roots of *Gelsemium sempervirens*, Aiton, commonly known as the "yellow jessamine."

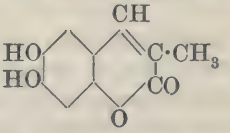
The medicinal value of the plant is due to the presence of certain alkaloids, only one of which, however, has been obtained in a crystalline condition.

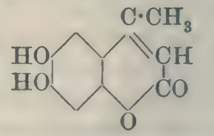
Among the earlier investigations of gelsemium there may be noted that of Wormley (*Amer. J. Pharm.*, 1870, **42**, 1), who isolated an impure alkaloidal product to which he gave the name of "gelsemine." This base was afterwards investigated by Sonnenschein (*Ber.*, 1876, **9**, 1182) and Gerrard (*Pharm. J.*, 1883, **13**, [iii], 641), who assigned to it the formulæ $C_{22}H_{38}O_4N_2$ and $C_{24}H_{28}O_4N_2$ respectively. The last-mentioned investigator was the first to obtain gelsemine and its salts in a crystalline state. Thompson (*Jahresber.*, 1887, 2218), who ascribed to gelsemine the formula $C_{54}H_{69}O_{12}N_4$, showed that it was accompanied in the plant by a second alkaloid, which he obtained in an amorphous condition, and which he designated as "gelseminine." Both gelsemine and gelseminine have more recently been examined by Cushny (*Ber.*, 1893, **26**, 1725), who proposed the formulæ $C_{49}H_{63}O_{14}N_5$ and $C_{42}H_{47}O_{14}N_3$ respectively for the two bases. Spiegel (*Ber.*, 1893, **26**, 1045) suggested the formula $C_{22}H_{26}O_3N_2$ for the crystalline base, which was confirmed by Gœldner (*Ber. deut. pharm. Ges.*, 1895, **5**, 330), who obtained it in colourless crystals, melting at 160°.

Some confusion has arisen as to the nomenclature of the two bases isolated from gelsemium; thus in the English literature the crystalline base is referred to as gelsemine, and the amorphous product as gelseminine, whilst most of the German investigators, for example, Spiegel (*loc. cit.*) and Gœldner (*loc. cit.*), use these names in the opposite sense. In this communication the English nomenclature is adhered to.

The present investigation has resulted in the isolation of the alkaloid gelsemine in a pure crystalline condition. The base is found to melt considerably higher than has hitherto been recorded (m. p. 178°, instead of 160°), and it has been conclusively shown to possess the formula $C_{20}H_{22}O_2N_2$. Besides gelsemine and gelseminine, the presence of a third alkaloidal substance in gelsemium has been established. This substance is weakly basic and amorphous, but possesses strongly toxic properties.

It was shown by Wormley (*loc. cit.*) that gelsemine was accompanied in the plant by an acidic substance, which he called "gelseminic acid," an observation which has been confirmed by the present author. Gelseminic or "gelsemic" acid has been shown by Schmidt (*Arch. Pharm.*, 1898, **236**, 236) to be a monomethyl ether of æsculetin (4 : 5-dihydroxycoumarin). Two æsculetin monomethyl ethers are known, which have been incorrectly termed α- and β-methylæsculetin respectively (compare *Beilstein's Handbuch*, III., 568), the compound from gelsemium having been given by Schmidt the latter designation. It is evident, however, that the names α- and β-methylæsculetin can only be correctly applied to substances possessing the following formulæ respectively (Pechmann and Kraft, *Ber.*, 1901, **34**, 423):





Gelseminic acid is, therefore, æsculetin 4-(or-5)monomethyl ether, and it is considered desirable to retain for this substance the name "scopoletin," as proposed by Eykman (*Rec. trav. chim.*, 1884, **3**, 171), who first obtained it from the rhizome of *Scopolia japonica*. The fluorescent substance, known as β-methylæsculetin, which is contained in the bark of *Prunus serotina* and in jalap (Trans., 1909, **95**, 243; *J. Amer. Chem. Soc.*, 1910, **32**, 93) would accordingly be more appropriately termed scopoletin.

A summary of the results of the complete investigation of gelsemium, is given at the end of this paper.

EXPERIMENTAL.

The material employed in this investigation consisted of the dried rhizome and roots of *Gelsemium sempervirens*, Aiton.

A portion (20 grams) of the crushed drug was extracted successively in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 35—50°)	extracted	0·39 gram	=	1·95 per cent.
Ether	,,	0·16 ,,		0·80 ,,
Chloroform	,,	0·34 ,,		1·70 ,,
Ethyl acetate	,,	0·16 ,,		0·80 ,,
Alcohol	,,	1·63 ,,		8·15 ,,
Total		2·68 grams	=	13·40

For the purpose of a complete examination, 49·44 kilograms of the ground material were completely extracted with hot alcohol. After the removal of the greater portion of the alcohol, a viscid, dark-coloured extract was obtained, amounting to 9·20 kilograms.

Distillation of the Extract with Steam.

A quantity (2 kilograms) of the above-mentioned extract, representing about 10·75 kilograms of the drug, was mixed with water, and steam passed through the mixture for some hours. The distillate, which amounted to 5 litres, contained some drops of oil floating on the surface. It was extracted with ether, the ethereal liquid being dried and the solvent removed, when a small quantity of an essential oil was obtained. This was a very pale yellow liquid, and amounted to about 2 grams, being thus equivalent to about 0·019 per cent. of the weight of the drug.

Non-volatile Constituents of the Extract.

After the distillation of the extract with steam, as described above, there remained in the distillation flask a quantity of a brown resin (A) and a dark-coloured aqueous liquid (B). The resin was collected, and repeatedly washed with water until nothing further was removed, the washings being added to the above-mentioned aqueous liquid.

This resin was a brown, viscid solid, and amounted to 412 grams. It was dissolved in alcohol and mixed with purified sawdust, the thoroughly dried mixture being then successively extracted in a Soxhlet apparatus with petroleum (b. p. 35—50°), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin (A).

Isolation of Pentatriacontane, $C_{35}H_{72}$, *and Emodin Monomethyl Ether.*

The petroleum extract, which formed a brown, semi-liquid mass and amounted to 224 grams, was dissolved in 2 litres of warm ether and the solution kept for some days, when a small quantity of an almost colourless substance separated. This was collected and washed with a little ether, after which it was distilled under diminished pressure. The distillate, which rapidly solidified, was crystallised from ethyl acetate, when it was obtained in small, colourless, glistening leaflets, melting at 75°. (Found, C = 84·9; H = 14·5. Calc., C = 85·4; H = 14·6 per cent.)

This substance was therefore pentatriacontane.

The ethereal liquid, from which the pentatriacontane had been removed as above described, was extracted with successive portions of an aqueous solution of sodium carbonate, and finally washed with water. The alkaline liquids and washings were united, acidified, and extracted with ether, when 15 grams of a viscid, oily liquid were obtained. On distilling this liquid under diminished pressure, it passed over between 245° and 255°/25 mm., and then became almost solid. It consisted of a mixture of fatty acids, which were examined in connexion with a similar product obtained from the non-acidic portion of the petroleum extract after its hydrolysis.

The ethereal liquid, from which the pentatriacontane and free fatty acids had been removed, as above described, was subsequently shaken with a solution of sodium hydroxide. The alkaline extracts, which had assumed a red colour, were acidified and extracted with ether, when a very small quantity of an orange-yellow substance was obtained. This when crystallised from ethyl acetate formed orange-red prisms, which melted at about 190°, and when mixed with a little emodin monomethyl ether, fusion occurred at the same temperature. The quantity so obtained was too small for analysis, but the substance appeared to be emodin monomethyl ether (m. p. 195°), since on heating for a short time with concentrated sulphuric acid it gave a substance soluble in aqueous sodium carbonate and agreeing in its properties with emodin.

Isolation of a Phytosterol, $C_{27}H_{46}O$.

The ethereal liquid which had been extracted with alkalis, as above described, was evaporated, when a quantity of an oily product was obtained. This was hydrolysed by heating with an alcoholic solution of potassium hydroxide, the alcohol removed, water added, and the alkaline liquid extracted with ether. The ethereal solution was washed, dried, and the solvent removed, when a quantity of brown resinous material was obtained. This was extracted with cold absolute alcohol, in which only a small portion dissolved. The alcoholic solution was concentrated, and a little water added, when, on keeping, a substance separated in flat needles, which after recrystallisation from a mixture of dilute alcohol and ethyl acetate formed glistening, flat needles, melting at 136°. The amount of this substance was 1·5 grams:

0·1600, on heating at 110°, lost 0·0072 H_2O. $H_2O = 4·5$.
0·1336* gave 0·4110 CO_2 and 0·1455 H_2O. $C = 83·9$; $H = 12·1$.
$C_{27}H_{46}O,H_2O$ requires $H_2O = 4·5$ per cent.
$C_{27}H_{46}O$ requires $C = 83·9$; $H = 11·9$ per cent.

This substance thus agrees in composition with a phytosterol, and it yielded the colour reaction of that class of compounds. A determination of its rotatory power gave the following result:

* Anhydrous substance.

0·2393, made up to 20 c.c. with chloroform, gave α_D $-0°58'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-40·4°$.

The *acetyl* derivative, when crystallised from acetic anhydride, separated in needles melting at 125—127°.

The brown resinous material, from which the phytosterol had been removed by extraction with alcohol, as above described, was thoroughly examined, but nothing definite could be isolated from it. It appeared to consist of a mixture of hydrocarbons.

Identification of the Fatty Acids.

The alkaline aqueous solution of potassium salts, from which the phytosterol had been removed by extraction with ether, as above described, was acidified and again extracted with ether, the ethereal solution being washed, dried, and the solvent removed. A quantity (10 grams) of fatty acids was thus obtained, which, when distilled under diminished pressure, passed over between 240° and 260°/25 mm. As these acids distilled within the same range of temperature as those previously obtained, which existed in the drug in the free state, for the purpose of their examination the two portions were mixed.

Twenty grams of the mixed acids were converted into their lead salts, and the latter digested with ether, when a portion dissolved. Both the soluble and insoluble portions were decomposed by hydrochloric acid, and the regenerated fatty acids purified by distillation under diminished pressure. The soluble portion of the lead salts yielded 11 grams of liquid acids, while the insoluble portion gave 8 grams of solid acids.

The Liquid Acids.—These acids, when distilled under diminished pressure, passed over at about 225°/15 mm. An analysis and a determination of the iodine value gave the following results:

0·1430 gave 0·4030 CO_2 and 0·1518 H_2O. C = 76·8; H = 11·8.

0·4224 absorbed 0·6783 iodine. Iodine value = 160.

$C_{18}H_{34}O_2$ requires C = 76·6; H = 12·1 per cent. Iodine value = 90·1.
$C_{18}H_{32}O_2$ " C = 77·1; H = 11·4 " " " = 181·4.

In order to obtain more definite information respecting the nature of the above mixture, a quantity of it was oxidised according to the method described by Lewkowitsch (*Chemical Technology and Analysis of Oils, Fats, and Waxes*, 1904, Vol. I., p. 360). This resulted in the formation of tetrahydroxystearic acid (m. p. 157—160°) and a small quantity of dihydroxystearic acid (m. p. 125—127°). It may thus be concluded that the liquid acids consisted chiefly of a mixture of oleic and linolic acids, the latter in predominating amount.

The Solid Acids.—These acids melted at about 55°, and on analysis gave the following result:

0·1383 gave 0·3842 CO_2 and 0·1590 H_2O. C = 75·8 ; H = 12·7.

$C_{16}H_{32}O_2$ requires C = 75·0 ; H = 12·5 per cent.
$C_{18}H_{36}O_2$,, C = 76·1 ; H = 12·7 ,,

From this result it would appear that the solid acids consisted of a mixture of palmitic and stearic acids, the latter predominating.

Ethereal Extract of the Resin.

Isolation of Ipuranol, $C_{23}H_{38}O_2(OH)_2$.

This extract was a brown, amorphous mass, and amounted to 10 grams. It was redissolved in about 500 c.c. of warm ether and kept for some days, when a small quantity of an almost colourless, amorphous substance separated. This was collected and crystallised from a mixture of pyridine and dilute alcohol, when it formed microscopic needles, melting at 290°. (Found, C = 72·3 ; H = 10·5. Calc., C = 72·6 ; H = 10·5 per cent.)

This substance was thus identified as ipuranol, and when treated with sulphuric acid and acetic anhydride it yielded the colour reaction shown by this compound. From it was also prepared diacetylipuranol, which separated from acetic anhydride in glistening leaflets, melting at 162°.

The ethereal solution from which the ipuranol had been separated, as above described, was examined, but nothing definite was isolated from it.

The chloroform, ethyl acetate, and alcohol extracts of the resin amounted to 35, 36, and 95 grams respectively, and consisted entirely of amorphous products.

Examination of the Aqueous Liquid (B).

Isolation of Scopoletin.

This liquid, as already indicated, represented that portion of the original alcoholic extract of the drug which was soluble in cold water, and from which the previously-described resin (A) had been removed.

It was thoroughly extracted with chloroform, these extracts being washed, dried, and the solvent removed. A quantity (about 5 grams) of a crystalline compound was thus obtained, which, after recrystallisation from alcohol, formed long, almost colourless needles, melting at 204°. Its alkaline solution showed a fine blue fluorescence.

0·1430 gave 0·3286 CO_2 and 0·0550 H_2O. C = 62·6 ; H = 4·2.

$C_{10}H_8O_4$ requires C = 62·5 ; H = 4·2 per cent.

A methoxyl determination by means of Perkin's modification of the Zeisel method gave the following result:

0·2132 gave 0·2584 AgI. OMe = 16·0.

$C_9H_5O_3{\cdot}OMe$ requires OMe = 16·1 per cent.

The substance is thus identified as scopoletin, a methyl ether of æsculetin.

Its acetyl derivative separates from acetic anhydride in colourless leaflets, melting at 177°.

Dibromoscopoletin, $C_{10}H_6O_4Br_2$.—Five grams (six atoms) of bromine were added to a solution of scopoletin (2 grams) in about 50 c.c. of chloroform. Hydrogen bromide was slowly evolved, but the liquid did not become colourless. After keeping some hours, a crystalline substance separated, which was removed and recrystallised from alcohol, when it formed yellow, glistening plates, melting at 249°:

0·1682 gave 0·1800 AgBr. Br = 45·5.

$C_{10}H_6O_4Br_2$ requires Br = 45·7 per cent.

This substance is therefore a *dibromoscopoletin.*

Dibromoscopoletin is sparingly soluble in ether, chloroform, or alcohol, and its solution in alkalis shows a very intense green fluorescence.

The two bromine atoms in dibromoscopoletin appear to be in the benzene nucleus, as this substance instantly decolorises a cold alkaline solution of potassium permanganate, and, therefore, still contains a double linking. In this respect it resembles the dibromocoumarin described by Perkin (Trans., 1870, **23**, 371).

On heating dibromoscopoletin with acetic anhydride, it is readily acetylated. The *acetyl* derivative forms colourless prisms, melting at 224°.

Isolation of Gelsemine, $C_{20}H_{22}O_2N_2$.

The aqueous liquid from which the scopoletin had been removed, as above described, was extracted with successive portions of amyl alcohol. This, however, only removed small quantities of an amorphous nitrogenous product, which was non-basic, and from which nothing definite could be isolated. The liquid was accordingly rendered alkaline with sodium carbonate and thoroughly extracted with ether, the combined ethereal extracts being washed, dried, and the solvent removed. A quantity of a pale yellow product was thus obtained, which crystallised very readily from acetone in handsome, glistening prisms, melting at 175—178°. After recrystallisation from the same solvent, its melting point was constant at 178°. The quantity isolated amounted to 12 grams. It gave all the usual reactions characteristic of alkaloids:

1·1448, when heated at 120°, lost 0·1774 acetone. $C_3H_6O = 15·5$.
0·1594* gave 0·4353 CO_2 and 0·0980 H_2O. $C = 74·5$; $H = 6·8$.
0·3458* „ 27·5 c.c. N_2 at 27° and 754 mm. $N = 8·7$.
$C_{20}H_{22}O_2N_2$ requires $C = 74·5$; $H = 6·8$; $N = 8·7$ per cent.
$C_{20}H_{22}O_2N_2,C_3H_6O$ requires $C_3H_6O = 15·3$ per cent.

This substance, therefore, corresponds with the crystalline alkaloid, gelsemine, which has previously been isolated from gelsemium, and for which, as already mentioned, several empirical formulæ have been suggested. The fact that gelsemine crystallises from acetone with one molecule of this solvent (see above) was confirmed by mixing 1 gram of the air-dried preparation with 20 c.c. of water and distilling the liquid. On adding *p*-bromophenylhydrazine to the distillate, a crystalline precipitate was formed, melting at 93°, which corresponded in all respects with acetone-*p*-bromophenylhydrazone.

The molecular weight of gelsemine was determined by the cryoscopic method in acetic acid solution:

0·5250*, in 24·90 acetic acid, gave $\Delta t = -0·270°$. M.W. = 305.
$C_{20}H_{22}O_2N_2$ requires M.W. = 322.

In benzene solution association occurs, and numbers corresponding with twice this molecular weight are obtained:

0·6340*, in 20·70 benzene, gave $\Delta t = -0·248°$. M.W. = 605.
$(C_{20}H_{22}O_2N_2)_2$ requires M.W. = 644.

In order to ascertain whether gelsemine is homogeneous, a quantity was converted into its hydrochloride, and this salt recrystallised, first from dilute alcohol and then from water. The base was then regenerated, and, after crystallisation from acetone, again analysed:

0·1414* gave 0·3866 CO_3 and 0·0880 H_2O. $C = 74·5$; $H = 6·9$.
$C_{20}H_{22}O_2N_2$ requires $C = 74·5$; $H = 6·8$ per cent.

For further confirmation of the purity of the material, the base was converted into its nitrate. This salt, which forms glistening prisms, melting above 280°, was recrystallised from water, and the base regenerated from it. The product so obtained, after crystallisation from acetone, gave the following results on analysis:

0·1462* gave 0·3980 CO_2 and 0·0906 H_2O. $C = 74·2$; $H = 6·8$.
$C_{20}H_{22}O_2N_2$ requires $C = 74·5$; $H = 6·8$ per cent.

The formula of the base deduced from these analyses is in harmony with the result obtained from the analysis of the hydrochloride.

Gelsemine forms a monohydrochloride crystallising in small prisms, melting indefinitely at about 300°:

0·5614 gave 0·2310 AgCl. $Cl = 10·1$.
$C_{20}H_{22}O_2N_2,HCl$ requires $Cl = 9·9$ per cent.

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* Constant at 120°.

A determination of its specific rotatory power gave the following result:

0·3100, made up to 20 c.c. with water, gave $[\alpha]_D + 0°5'$ in a 2-dcm tube, whence $[\alpha]_D + 2·6°$.

The close agreement of these results shows conclusively that the empirical formula of gelsemine is $C_{20}H_{22}O_2N_2$.

A determination of its specific rotatory power gave the following result:

0·4066*, made up to 20 c.c. with chloroform, gave $[\alpha]_D + 0°39'$ in a 2-dcm. tube, whence $[\alpha]_D + 15·9°$.

Examination of the Amorphous Alkaloidal Products.

The alkaline, aqueous liquid from which the gelsemine had been removed by extraction with ether, as above described, was repeatedly extracted by means of amyl alcohol, when a relatively small quantity of an amorphous, basic product was obtained. This appeared to consist of a mixture, and two alkaloidal products were found to be present, one of which was much more strongly basic than the other. It was dissolved in chloroform, and extracted several times with 1 per cent. aqueous hydrochloric acid, which removed the more strongly basic product. The material obtained on rendering the acid extracts alkaline was isolated by means of chloroform, when it formed an amorphous, brown-coloured product. Neither the free base nor any of its salts could be obtained in a crystalline condition. This more strongly basic product appears to correspond with the amorphous alkaloid to which the name "gelseminine" has been given.

The chloroform solution from which the "gelseminine" had been removed by means of 1 per cent. acid, as above described, was shaken many times with 10 per cent. aqueous sulphuric acid, which slowly removed a small quantity of a very weakly basic substance. As in the case of "gelseminine," neither the free base nor its salts could be obtained in a crystalline condition. This substance responds to the usual alkaloid reagents, but appears to be stable only in the form of its salts, as on keeping a chloroform solution of the base for some time the product becomes insoluble in acids.

The alkaline aqueous liquid from which the alkaloidal products had been removed, as above described, was neutralised by means of acetic acid and treated with a solution of basic lead acetate. This produced a voluminous yellow precipitate, which was collected, washed, and then suspended in water and decomposed by hydrogen sulphide. On filtering the mixture, a liquid was obtained which gave a bluish-black coloration with ferric chloride, and evidently contained a quantity of tannin, but no definite products could be isolated from it.

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* Constant at 120°.

The filtrate from the basic lead acetate precipitate was treated with hydrogen sulphide for the removal of the excess of lead, and the filtered liquid concentrated under diminished pressure to a volume of about 2 litres. The concentrated liquid contained a considerable quantity of a sugar, as it readily reduced Fehling's solution, and yielded *d* phenylglucosazone, melting at 208—210°.

One-fifth of the total liquid was diluted with water to 1 litre, about 50 grams of concentrated sulphuric acid, diluted with an equal weight of water, added, and the liquid repeatedly extracted with chloroform with the object of isolating any organic acids present. As this operation removed only a small quantity of acetic acid, the acid aqueous liquid was boiled for an hour and again extracted with chloroform, when nearly a gram of scopoletin was obtained. It thus appears probable that a glucoside of scopoletin was present in the original aqueous liquid, but all attempts to isolate this substance were unsuccessful.

Physiological Tests.

The following physiological tests were conducted in the Wellcome Physiological Research Laboratories by Dr. H. H. Dale, to whom the author now wishes to express his thanks:

A quantity (0·1 gram) of gelsemine hydrochloride, when injected intravenously into a rabbit, caused practically no effect, a result which is in agreement with an observation by Cushny.

One milligram of the hydrochlorides of both the amorphous bases, when injected intravenously into rabbits, caused death from respiratory failure in about twenty-five minutes, preceded by convulsions.

Summary.

The results of this investigation may be summarised as follows:

The material employed consisted of the dried rhizome and roots of *Gelsemium sempervirens*, Aiton.

An alcoholic extract of the drug, when distilled with steam, yielded a small amount of an essential oil. The non-volatile constituents, as obtained after treating the alcoholic extract with steam, consisted of a brown resin insoluble in water, and material which remained dissolved in the cold aqueous liquid. The resin, amounting to about 3·8 per cent. of the weight of the drug, yielded pentatriacontane; traces of emodin monomethyl ether; a phytosterol, $C_{27}H_{46}O$ (m. p. 136°; $[\alpha]_D$ $-40{\cdot}4°$); a small amount of ipuranol, $C_{23}H_{38}O_2(OH)_2$; and a mixture of fatty acids, consisting of palmitic, stearic, oleic, and linolic acids. The portion of the alcoholic extract of the drug which was soluble in water, and from which the above-described resin had been removed, contained scopoletin (a monomethyl ether of æsculetin), which was present in the free state, and also in the form of a glucoside, together with a quantity of sugar. It yielded, furthermore, three alkaloidal products, one of which, gelsemine, has been obtained in a pure crystalline state, melting considerably higher than has hitherto been recorded (178°, instead of 160°), and which has been conclusively shown to possess the formula $C_{20}H_{22}O_2N_2$. The other alkaloidal products, one of which corresponds with the so-called "gelseminine" of Thompson (*loc. cit.*) and Cushny (*loc. cit.*), were amorphous, and no crystalline derivative could be obtained from them.

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London.

CCXXXIII.—*The Distillation of Mixtures of Enantiomorphously Related Substances.*

By William Charles Evans.

Although most of the possible types of behaviour which can arise during the distillation of mixtures have been experimentally studied, one of the simplest appears hitherto to have escaped investigation. This type is the one in which the two components of the liquid mixture have the same boiling point under all the pressures dealt with, and in which the boiling points of mixtures of all compositions are identical with those of the components under the same pressure. Under these conditions it would be expected that all mixtures of the two components should behave on distillation like a single substance; the composition of the vapour should be the same as that of the liquid even when the pressure is varied, and no separation by fractional distillation should be possible.

Probably the only instances in which conditions of this highly specialised character can be experimentally realised are to be found amongst mixtures of enantiomorphously related substances, and in the study of such cases the delicate nature of the method available for determining the composition of the mixtures greatly facilitates the practical examination. It is, of course, well known that no separation of the optically active components of an externally compensated substance can be effected by fractional distillation; but it has not previously been shown and is not immediately evident that mixtures of two enantiomorphously related isomerides in any casual proportion would resist separation by fractional distillation. The following observations of the behaviour of optically active mixtures of *d*- and *l*-camphor and also of *d*- and *l*-tetrahydroquinaldine were made at the suggestion of Professor Pope for the purpose of obtaining the lacking experimental data.

A. *Distillation of Mixtures of* d- *and* l-*Camphor.*

The mixtures were prepared from natural *d*-camphor and artificially prepared externally compensated camphor in suitable proportions. In the following series of experiments, the camphor was distilled from a retort heated by a naked flame, care being taken to prevent the distillate from solidifying in the neck of the retort; the distillate was collected in a number of fractions, and the specific rotatory power of each determined in benzene solution.

(1) *d*-Camphor alone was distilled, and the specific rotatory powers of the first and last fractions of the distillate, in 10 per cent. solutions, found to be $[\alpha]_D$ +40·85° and +40·95° respectively; these values are identical within the limits of experimental error.

(2) On distilling externally compensated camphor in the same manner, the first and last fractions were found to be optically inactive.

(3) A mixture consisting approximately of one part of *l*-camphor and two parts of *d*-camphor was separated into five fractions by distillation as above described under atmospheric pressure; the specific rotatory powers of the five fractions in 8 per cent. benzene solution were $[\alpha]_D$ +27·15°, +27·02°, +27·37°, +26·66°, and +26·14° respectively. A similar distillation was performed with another mixture, and yielded five fractions with the specific rotatory powers $[\alpha]_D$ +21·40°, +20·09°, +19·75°, +20·21°, and +20·05° respectively. It will be noted that the rotatory powers of the five fractions composing either series are not identical within the limits of experimental error, so that some slight degree of separation is indicated. In these determinations, however, no special precautions were taken to ensure thorough admixture of the two components before distillation; it therefore seemed possible that, owing to the readiness with which camphor sublimes, the two components, present in the solid state in different quantities, might have sublimed at different rates determined by the surface exposed and the temperature attained by the solid.

(4) The contingency just indicated was obviated by melting together the mixtures of *d*- and *l*-camphor before introducing them into the retort; after taking this precaution, one mixture, similar to those examined in (3), gave five fractions, of which the specific

rotatory powers in 8 per cent. solutions were $[\alpha]_D$ + 20·24°, + 20·56°, + 20·55°, + 20·60°, and + 20·56° respectively. These five values are identical within the limits of experimental error, and it is thus indicated that intimate mixtures of *d*- and *l*-camphor cannot be altered in composition by distillation under atmospheric pressure.

B. *Distillation of Mixtures of* d- *and* l-*Camphor in Steam.*

(5) A mixture prepared from *d*-camphor and externally compensated camphor, and consisting of about two parts of *d*-camphor and one of *l*-camphor, was distilled in a current of steam, three fractions being collected; these, and the residue left in the distilling flask, were collected and dried in the air. The three fractions and the residue gave the specific rotatory powers, in 4 per cent. benzene solution, of $[\alpha]_D$ + 16·44°, + 15·24°, + 14·55°, and + 27·90° respectively; repetition of the operation with another similar mixture yielded four fractions and a residue, which gave the specific rotatory powers of $[\alpha]_D$ + 15·95°, + 14·28°, + 14·15°, + 14·49°, and + 27·15° respectively. No precautions were taken to ensure intimate admixture of the *d*- and *dl*-camphor previous to the steam distillation, and the variations in the specific rotatory power of the distillate and the large difference between these values and those referring to the residues left in the distilling flask might, it was anticipated, be due to differences in the rate of sublimation in steam of the solid active and externally compensated substances.

(6) That the cause just suggested of the variable rotatory powers of the distillate and residue is the true one was demonstrated by the following trials. A mixture of approximately one part of *d*-camphor and two parts of externally compensated camphor was melted and allowed to solidify, then roughly ground, and subjected to steam distillation as described under (5). The three fractions of camphor which distilled and the residue which remained in the still, examined in 5 per cent. benzene solution, gave the specific rotatory powers $[\alpha]_D$ + 21·54°, + 21·26°, + 21·62°, and + 21·55° respectively.

The close approximation to constancy of these numbers shows that mixtures of *d*- and *l*-camphor, if care is take to ensure intimate admixture, behave like a single substance on distillation in a current of steam.

C. *Distillation of Mixtures of* d- *and* l-*Tetrahydroquinaldine.*

As indicated in the previous pages, the investigation of the problem under consideration with the aid of mixtures of *d*- and *l*-camphor is complicated by the fact that these substances are solid at the ordinary temperatures, and that their melting and boiling points do not differ greatly. Further information was therefore sought from the study of mixtures of *d*- and *l*-tetrahydroquinaldine.

Externally compensated tetrahydroquinaldine was treated with *d*-α-bromocamphor-π-sulphonic acid, and the lævo-component of the base in large measure separated by Pope and Peachey's method (Trans., 1899, **75**, 1068); the mixture of the *d*-base with a small proportion of the *l*-isomeride remaining after the separation of the *l*-tetrahydroquinaldine *d*-α-bromocamphorsulphonate was isolated by distilling the mother liquors in a current of steam after addition of lime. Such mixtures were used in the following series of experiments.

(7) Two specimens of the mixed *d*- and *l*-tetrahydroquinaldine, containing (*a*) about 75 per cent. of *d*- and 25 per cent. of *l*-tetrahydroquinaldine, and (*b*) about 56 per cent. of *d*- and 44 per cent. of *l*-tetrahydroquinaldine, were distilled from Wurtz flasks under a pressure of 300 mm. of mercury. The rotatory powers, α_D, of the several fractions collected were determined in 100 mm. tubes at 16°:

	(*a.*)	(*b.*)
Fractions.	α_D.	α_D.
1	+28·39°	+6·85°
2	28·47	6·87
3	28·48	6·87
4	28·46	6·89
5	28·41	6·87
6	28·44	6·88
7	28·43	6·87
8	28·47	
9	28·49	

(8) Two specimens of the mixed bases containing (*c*) about 65 per cent. of *d*- and 35 per cent. of *l*-tetrahydroquinaldine, and (*d*) and (*e*) about 78 per cent. of *d*- and 22 per cent. of *l*-tetrahydroquinaldine, were distilled from a Wurtz flask over a naked flame, (*c*) under pressures increased gradually from 55 to 415 mm. of mercury, (*d*) under atmospheric pressure, and (*e*) under pressures which were caused to rise and fall during distillation between 140 and 600 mm. of mercury. The rotatory powers observed in 100 mm. tubes of the various fractions collected are stated in the appended table:

	(*c.*)	(*d.*)	(*e.*)
Fractions.	α_D.	α_D.	α_D.
1	+11·34°	+33·42°	+33·40°
2	11·39	33·43	33·38
3	11·40	33·46	33·39
4	11·38	33·45	33·45
5	11·40	33·42	33·39
6	11·38	33·46	33·45
7	11·39		
8	11·36		
9	11·39		
10	11·39		

From the above results, it is to be concluded that on distilling mixtures of enantiomorphously related compounds under varying conditions of pressure, no difference in composition is to be observed between the various fractions of the distillate by determination of the rotatory powers, and that therefore no separation of such mixtures into their optically active components is possible by distillation. The fact that no change in rotatory power can be detected in partly compensated mixtures of either *d*- and *l*-camphor or *d*- and *l*-tetrahydroquinaldine on fractional distillation may doubtless be regarded as a demonstration that under the conditions prevailing during distillation no combination of a racemic character exists between the enantiomorphously related isomerides.

The above are the first recorded instances of the theoretically simplest case arising in the distillation of mixtures, but no doubt such instances could be easily multiplied amongst other mixtures of enantiomorphously related compounds.

THE CHEMICAL LABORATORY,
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CCXXXIV.—*The Tertiary Acidic and Alkyl Derivatives of* d-*Camphorimide.*

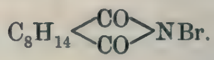
By WILLIAM CHARLES EVANS.

ALTHOUGH it is generally recognised that phthalic acid and camphoric acid exhibit striking analogies in chemical behaviour, the similarities existing between the two acids have not previously been traced in the reactions of their imides. At the suggestion of Professor W. J. Pope, I have therefore endeavoured to ascertain to what extent the reactions by means of which the imidogen hydrogen atom in phthalimide can be replaced by halogen atoms and by alkyl groups are capable of effecting similar substitutions in *d*-camphorimide; that a very deep-rooted analogy in chemical behaviour exists between the two acid imides will be evident from the description of the modes of preparation of the compounds described below.

Preparation of d-*Camphorimide.*

A comparison of the various methods which have been described for the preparation of *d*-camphorimide showed that a method identical in principle with that given by Bredt (*Annalen*, 1903, **328**, 344) is the most convenient for use in the preparation of this substance. *d*-Camphoric acid is gently boiled in a retort provided with a long and wide-necked retort heated in a metal-bath; at the same time a brisk current of dry ammonia gas is passed through the boiling acid from a steel storage cylinder. After the evolution of water vapour has completely ceased, the material is distilled, and, in order to ensure that no camphoric anhydride has escaped conversion, the distillate is once more distilled in a current of ammonia gas. The *d*-camphorimide thus obtained is practically pure, and, after crystallisation from dilute alcohol, melts at 243°.

d-*Camphorbromoimide*,



$$C_8H_{14}{<}\begin{matrix}CO\\CO\end{matrix}{>}NBr.$$

To a cold solution of 12·3 grams of *d*-camphorimide and 2·7 grams of sodium hydroxide in 125 c.c. of water is gradually added a well-cooled solution of 11 grams of bromine in 250 c.c. of water; a white, crystalline substance immediately separates, which, after collection and crystallisation from benzene, is obtained in minute, white crystals, melting at 154°. The compound thus obtained dissolves readily in chloroform, acetone, ether, or ethyl acetate, and is less soluble in alcohol or benzene. It is decomposed by hydriodic acid in accordance with the equation:

$$C_{10}H_{14}O_2{:}NBr + 2HI = C_{10}H_{14}O_2{:}NH + HBr + I_2,$$

and, in accordance with this reaction, its analysis was effected by dissolving a weighed quantity in chloroform, to which a little potassium iodide and acetic acid had been added, and titrating the liberated iodine with thiosulphate solution:

0·1856 required 15·4 c.c. thiosulphate (1 c.c. = 0·02269 $Na_2S_2O_3,5H_2O$). Br = 30·36.

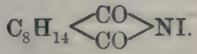
0·1822 gave 0·3086 CO_2 and 0·0930 H_2O. C = 40·20; H = 5·67.

$C_{10}H_{14}O_2NBr$ requires Br = 30·77; C = 40·16; H = 5·39 per cent.

The following determinations of rotatory power were made in 2·2-dcm. tubes at 18°:

Solvent.	Weight in 25 c.c.	α_D.	$[\alpha]_D$.
Benzene	0·4853 gram	+0·51°	+12·0°
,, ...	0·5960 ,,	0·587	11·2
,, ...	0·7707 ,,	0·81	12·0
Chloroform	0·4161 ,,	0·512	13·6
,, ...	0·6843 ,,	0·785	13·0
,, ...	0·7160 ,,	1·29	12·8

The substance is not completely stable in moist air, and to this must be attributed the slight variations in specific rotatory power obvious above.



d-*Camphoriodoimide*, $C_8H_{14}<\begin{smallmatrix}CO\\CO\end{smallmatrix}>NI$.

d-Camphorimide (5 grams, 1 mol.) and sodium hydroxide (1·3 grams, 1 mol.) are dissolved in water (350 c.c.), and the resulting solution added slowly and with vigorous stirring to a well-cooled solution of iodine (3·5 grams, 1 mol.), sodium bromide (5 grams), and bromine (2·3 grams, 1 mol.) in water (50 c.c.). A greyish-black solid immediately separates, which, on stirring, becomes brown; after collection, washing, and drying in a vacuum, the substance is crystallised from hot benzene, from which it separates in minute, light yellow crystals, melting and decomposing at 207°. The iodo-derivative thus obtained is readily soluble in acetone, chloroform, or ether, but less soluble in alcohol or benzene. It reacts with hydriodic acid in accordance with the following equation:

$$C_{10}H_{14}O_2{:}NI + HI = C_{10}H_{14}O_2{:}NH + I_2,$$

and, in accordance therewith, the iodine was determined by dissolving a weighed quantity in chloroform, adding potassium iodide and acetic acid, and titrating with thiosulphate:

0·2458 required 17·25 c.c. thiosulphate (1 c.c. = 0·02269 $Na_2S_2O_3,5H_2O$. I = 40·76.

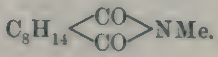
0·1632 gave 0·2330 CO_2 and 0·0717 H_2O. C = 38·94; H = 4·88.

$C_{10}H_{14}O_2NI$ requires I = 41·37; C = 39·09; H = 4·56 per cent.

The following determinations of rotatory power were made:

Solvent.	Weight in 25 c.c.	a_D.	$[a]_D$.
Chloroform	0·3852 gram	+0·514° in 2·2-dcm. tube.	+15·2°
,, ...	0·5130 ,,	0·690 ,, 2·2 ,,	15·3
,, ...	0·6448 ,,	0·406 ,, 1 ,,	15·7
,, ...	0·7468 ,,	0·470 ,, 1 ,,	15·7
Benzene	0·4055 ,,	0·260 ,, 1 ,,	16·0
,, ...	0·4383 ,,	0·280 ,, 1 ,,	16·0

The solutions in chloroform rapidly undergo decomposition and become deep violet in colour.

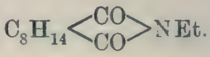


d-*Camphormethylimide*, $C_8H_{14}<\begin{smallmatrix}CO\\CO\end{smallmatrix}>NMe$.

The method of preparation of this substance described by Hoogewerff and van Dorp (*Rec. trav. chim.*, 1893, **12**, 13) may be conveniently replaced by the following simpler one. Camphorimide (5 grams) is dissolved in a mixture of 1·125*N*-potassium hydroxide (27·2 c.c., 1 mol.) and methyl iodide (4 grams); potassium iodide commences to separate in the cold, and the reaction is completed by heating for two hours on the water-bath. After separation of the potassium iodide and evaporation of the alcohol, the residue is dissolved in benzene; the benzene solution, an evaporation, yields a crystalline residue of *d*-camphormethylimide, which, when crystallised from aqueous alcohol, melts at 46°. Hoogewerff and van Dorp give the melting point as 40—42°. The substance is very soluble in most organic solvents. This compound may be also conveniently isolated from the mixture obtained by heating *d*-camphorimide, potassium hydroxide, and methyl iodide, by treatment with dilute sodium hydroxide solution in order to remove unchanged camphorimide, and crystallising the residue from dilute alcohol. The following determinations of rotatory power were made:

Solvent.	Weight in 25 c.c.	α_D in 2-dcm. tube.	$[\alpha]_D$.
Alcohol	0·6088 gram	+0·54 °	+11·1°
,, ...	0·7843 ,,	0·69	11·0
,, ...	0·8887 ,,	0·81	11·4
,, ...	1·0607 ,,	0·96	11·3
Acetone	0·7070 ,,	0·45	8·0
,, ...	1·0365 ,,	0·665	8·0

d-*Camphorethylimide*, $C_8H_{14}<\begin{matrix}CO\\CO\end{matrix}>NEt$.



d-Camphorimide (5 grams), 1·125*N*-potassium hydroxide (27·2 c.c.), and ethyl iodide (4·4 grams) were heated together on the water-bath for two hours; after filtration, the alcohol was evaporated off, and the residual sweet-smelling oil washed with dilute sodium hydroxide. The required ethyl derivative remained as an almost colourless solid, which crystallised from dilute alcohol in long, white needles, melting at 51—52°; the following determinations of rotatory power were made:

Solvent.	Weight in 25 c.c.	α_D in 2-dcm. tube.	$[\alpha]_D$.
Alcohol..............	0·5216 gram	+0·52°	+12·4°
,, ...	0·5370 ,,	0·54	12·6
,, ...	0·7588 ,,	0·76	12·5
,, ...	0·9757 ,,	0·955	12·5
Acetone	0·5886 ,,	0·395	8·4
,, ...	0·7348 ,,	0·52	8·8
,, ...	1·1890 ,,	0·81	8·5

Both the methyl and ethyl derivatives of *d*-camphorimide are practically inactive in benzene solutions.

d-*Camphorbenzylimide.*

This substance was obtained by Hoogewerff and van Dorp (*loc. cit.*) by heating benzylammonium camphorbenzylamate; it is more readily obtained by heating *d*-camphorimide (5 grams) with 1·125*N*-alcoholic potash (27·2 c.c.) and benzyl chloride (3·5 grams) on the water-bath for two hours, evaporating off the alcohol, and adding dilute sodium hydroxide. An almost quantitative yield of the solid product is obtained, which, after crystallisation from dilute alcohol, melts at 60—62°. The following determinations of rotatory power were made:

Solvent.	Weight in 25 c.c.	α_D in 2-dcm. tube.	$[\alpha]_D$.
Alcohol...............	0·4539 gram	+0·46°	+12·7°
,, ...	0·5776 ,,	0·56	12·1
,, ...	0·8032 ,,	0·78	12·1
Acetone	0·7067 ,,	0·67	11·9
,, ...	0·7388 ,,	0·71	12·0
,, ...	0·8361 ,,	0·815	12·2
,, ...	0·9848 ,,	0·94	11·9
Benzene	0·5476 ,,	0·23	5·2
,, ...	0·9557 ,,	0·37	4·8

As in the previous cases the specific rotatory power is much smaller in benzene than in alcohol or acetone solutions.

d-*Camphor*-p-*nitrobenzylimide*,

$C_8H_{14}<\genfrac{}{}{0pt}{}{CO}{CO}>N\cdot CH_2\cdot C_6H_4\cdot NO_2$.

Camphorimide (5 grams) dissolved in 1·125*N*-alcoholic potash (22·5 c.c.) was heated with *p*-nitrobenzyl chloride (4·75 grams) for a short time on the water-bath; after separating the alcohol and treating with dilute sodium hydroxide, the required derivative was obtained as a yellow solid, which, after crystallisation from alcohol, formed yellow needles, melting at 133°:

0·1985 gave 0·4709 CO_2 and 0·1142 H_2O. C = 64·69; H = 6·39.

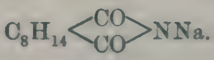
$C_{11}H_{20}O_4N_2$ requires C = 64·54; H = 6·33 per cent.

The following determinations of rotatory power were made:

Solvent.	Weight in 25 c.c.	α_D in 2-dcm. tubes.	$[\alpha]_D$.
Acetone	0·5071 gram	+0·48°	+11·8°
,, ...	0·6795 ,,	0·67	12·3
,, ...	0·7848 ,,	0·775	12·3
Benzene	0·5630 ,,	0·115	2·6
,, ...	0·9928 ,,	0·225	2·8

The rotatory power has again a smaller value in benzene than in acetone solutions.

d-*Camphorsodioimide*,



$C_8H_{14}<\genfrac{}{}{0pt}{}{CO}{CO}>NNa$.

This substance separates as a white, flocculent mass on warming a solution of sodium (0·63 gram) in alcohol (2 c.c.) and benzene (5 c.c.), with addition of *d*-camphorimide (5 grams) dissolved in benzene (20 c.c.); after collection and drying in a vacuum, the substance was analysed:

0·6025 gave 0·1990 Na_2SO_4. Na = 10·70.

$C_{10}H_{14}O_2NNa$ requires Na = 11·33 per cent.

The compound is readily soluble in water or alcohol, and is at once decomposed by acids.

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CCXXXV.—*Azomethineazo-dyes.*

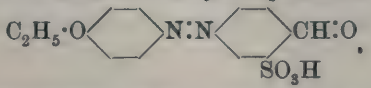
By Arthur George Green and Rajendra Nath Sen.

The azomethine group $\cdot CH\colon N\cdot$ lies between the azo-group $\cdot N\colon N\cdot$ and the stilbene group $\cdot CH\colon CH\cdot$, and in chromophoric power it also occupies an intermediate position. The objects of the present research were twofold, namely, first, to investigate the effect on the colour and dyeing properties of a compound containing both the azomethine and azo-groups, for example, whether such compounds would present similarities to the azostilbene dyes; and secondly, to ascertain how far the presence of auxochromic groups is necessary for the manifestation of dyeing properties in such compounds. In reference to the latter point it may be noted that it has been shown by Green and Crosland (Trans., 1906, **89**, 1602) that the dyes of the stilbene class are all azostilbene compounds containing no auxochromic group. Furthermore, dyes which contain no auxochrome are known in some other classes (for example, diamine-gold-yellow).

The method we have employed for preparing azomethineazo-dyes consists in acting on amino-compounds with an azo-aldehyde. As a convenient azo-aldehyde for the purpose, we have selected phenetoleazobenzaldehydesulphonic acid, $OEt\cdot C_6H_4\cdot N_2\cdot C_6H_3(SO_3H)\cdot CHO$, which is readily prepared by oxidation of the dye chrysophenin G with cold aqueous permanganate. By making use of this aldehyde, a number of azomethineazo-dyes have been prepared of varying degrees of complexity, and mostly containing no auxochromic group (unless the ethoxy-group can be considered as such). These are all yellow, crystalline compounds, which dye wool in yellow shades. Although tolerably strong dyes, their colouring power appears somewhat inferior to that of the azostilbene compounds. Affinity for cotton is only slightly developed, except in those cases in which a benzidine or analogous residue is present, and even then it is considerably weaker than in the stilbene series. The introduction of an auxochromic group (OH or NMe_2) has practically no effect on the dyeing properties, and does not increase the tinctorial power, augment the affinity, or change the shade. It is also remarkable that, whilst in the azo-series the introduction of more than one azo-group usually deepens the colour, with these compounds the shade seems almost independent of the number of azomethine groups in the molecule; thus the more complex compounds having two azo-groups and two azomethine groups possess nearly the same colour and tinctorial intensity as those with a single azo-group and a single azomethine group. On the other hand, when dissolved in concentrated sulphuric acid, differences of shade become apparent: those derived from aniline, aniline-*p*-sulphonic acid, and *p*-aminophenol dissolving with a yellowish red colour, those derived from benzidine and *p*-phenylenediamine with a crimson colour, and those derived from α- or β-naphthylamine with a violet colour. The members of this series which do not contain an auxochromic group possess in common with the dyes of the azostilbene class a considerable degree of fastness to alkalis, chlorine, and light. On the other hand, like other azomethine compounds, they are more or less unstable towards acids which tend to decompose them into the original aldehyde and amine.

EXPERIMENTAL.

Phenetoleazobenzaldehydesulphonic Acid,



This aldehyde was prepared by Green and Meyenberg's method (Eng. Pat. 1431 of 1898). One hundred grams of chrysophenin G conc. (Farbenfabriken vorm. F. Bayer & Co.), which is equivalent to about 92 grams of the pure dye,

$$OEt\cdot C_6H_4\cdot N_2\cdot C_6H_3(SO_3Na)\cdot CH{:}CH\cdot C_6H_3(SO_3Na)\cdot N_2\cdot C_6H_4\cdot OEt,$$

were dissolved in 6 litres of boiling water. Into this solution, cooled to 0—5° by addition of ice, was slowly run with rapid mechanical stirring a 3 per cent. solution of potassium permanganate until the colour of the latter was persistent (pale pink filtrate after saturating with sodium chloride). The quantity of permanganate required was 29 grams. After allowing to settle, the supernatant liquor was siphoned off, and the precipitate collected. The solution contained only a small quantity of aldehyde, which was isolated by salting out with potassium or sodium chloride. The main quantity of the aldehyde was contained in the precipitate in admixture with the manganese dioxide. In order to extract it, the precipitate was boiled two or three times with a litre of water, filtered from manganese dioxide, and potassium chloride added to the hot filtrate until precipitation was complete. The *potassium* salt of the aldehydesulphonic acid thus obtained was collected, washed with 50 per cent. alcohol, and dried. The yield was 81 grams, or 80 per cent. of the theoretical.*

The substance crystallises from water in orange-coloured, microscopic needles, sparingly soluble in cold, but readily so in hot, water. It reacts readily with phenylhydrazine, producing a reddish-orange *phenylhydrazone*. With sodium hydrogen sulphite solution, it gives a yellow, crystalline bisulphite compound. In concentrated sulphuric acid it dissolves with a red colour, which on dilution with water becomes yellow. The following results were obtained on analysis:

---

* The large yield obtained affords incidentally an additional proof of Richard Meyer's formula for chrysophenin (*Ber.*, 1903, **36**, 2970), and definitely establishes the absence of an auxochromic (OH) group in this dye.

Found, K = (I) 10·12, (II) 10·18. S = (I) 9·0, (II) 8·9.

$C_{15}H_{13}O_5N_2SK$ requires K = 10·48; S = 8·6 per cent.

An estimation of nitrogen carried out with the *barium* salt gave:

Found, N = 6·98.

$(C_{15}H_{13}O_5N_2S)_2Ba$ requires N = 6·97 per cent.

A determination of the aldehyde group was effected by titration with a standard solution of phenylhydrazine hydrochloride (containing 1 per cent. of the base) in the presence of sodium acetate, employing *p*-nitrobenzaldehydesulphonic acid as indicator (I). Another method (II) consisted in titrating with a 0·5 per cent. solution of benzidine hydrochloride, but the end point was not very sharp:

Found, CHO = (I) 7·65; (II) 6·73.

$C_{15}H_{13}O_5N_2SK$ requires CHO = 7·8 per cent.

For the preparation of the azomethine dyes, the same general method was employed in all cases. This consisted in mixing in molecular proportions a hot aqueous solution of the potassium salt of the aldehyde with a hot alcoholic or aqueous solution of the respective amine. A few drops of hydrochloric acid were afterwards added, and the mixture was boiled for a few minutes to complete the condensation. The solution was then neutralised with potassium carbonate and left to cool, and the product which separated was recrystallised from dilute alcohol. In some cases (aniline, *p*-nitroaniline, aminosalicylic acid, and *p*-phenylenedimethyldiamine) the amine was dissolved in dilute acetic acid, in which case the condensation completes itself without the addition of hydrochloric acid.

Condensation Product with Aniline: *Phenetoleazosulphobenzylideneaniline*, $OEt\cdot C_6H_4\cdot N{:}N\cdot C_6H_3(SO_3H)\cdot CH{:}N\cdot C_6H_5$.

The free acid forms an orange-yellow, crystalline precipitate. It dissolves in hot water to an orange-yellow solution, but is almost insoluble in cold water. It dyes wool a fast yellow from a neutral or acetic acid bath, but has no affinity for cotton:

Found, N = 10·39.

$C_{21}H_{19}O_4N_3S$ requires N = 10·27 per cent.

Condensation Product with Aniline-p-*sulphonic Acid*: *Phenetoleazosulphobenzylideneaniline*-p-*sulphonic Acid*, $OEt\cdot C_6H_4\cdot N{:}N\cdot C_6H_3(SO_3H)\cdot CH{:}N\cdot C_6H_4\cdot SO_3H$,

The *potassium* salt forms fine, reddish-orange needles, fairly soluble in cold, and readily so in hot, water. It dyes fast yellow shades on wool, but has no affinity for cotton:

Found, N = 7·58; K = 13·44.

$C_{21}H_{17}O_7N_3S_2K_2$ requires N = 7·43; K = 13·85 per cent.

Condensation Product with p-*Nitroaniline*: *Phenetoleazosulphobenzylidene*-p-*nitroaniline*, $OEt{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_3(SO_3H){\cdot}CH{:}N{\cdot}C_6H_4{\cdot}NO_2$.

The *potassium* salt crystallises in bright reddish-orange needles, readily soluble in hot, and fairly so in cold, water. It dyes wool in reddish-yellow shades from a neutral or acetic acid bath, but has no affinity for cotton:

Found, N = 11·12; K = 7·75.

$C_{21}H_{17}O_6N_4SK$ requires N = 11·38; K = 7·93 per cent.

Condensation Product with p-*Aminophenol*: *Phenetoleazosulphobenzylidene*-p-*aminophenol*, $OEt{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_3(SO_3H){\cdot}CH{:}N{\cdot}C_6H_4{\cdot}OH$.

The *potassium* salt forms fine orange needles, readily soluble in hot water. It dyes wool in reddish-yellow shades, but has no affinity for cotton:

Found, N = 9·04; K = 8·61.

$C_{21}H_{18}O_5N_3SK$ requires N = 9·07; K = 8·42 per cent.

Condensation Product with p-*Aminosalicylic Acid*: *Phenetoleazosulphobenzylideneaminosalicylic Acid*,

$OEt{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_3(SO_3H){\cdot}CH{:}N{\cdot}C_6H_3(OH){\cdot}CO_2H$.

The *potassium* salt crystallises in orange needles, readily soluble in hot, but sparingly so in cold, water. It dyes wool in reddish-yellow shades fast to alkalis, but only has a small affinity for cotton:

Found, N = 7·72; K = 13·98.

$C_{22}H_{17}O_7N_3SK_2$ requires N = 7·70; K = 14·31 per cent.

Condensation Product with p-*Phenylenedimethyldiamine*: *Phenetoleazosulphobenzylidene*-p-*phenylenedimethyldiamine*,

$OEt{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_3(SO_3H){\cdot}CH{:}N{\cdot}C_6H_4{\cdot}N(CH_3)_2$.

The *potassium* salt crystallises in water containing potassium carbonate in small leaflets of greenish lustre. It is fairly soluble in cold, and readily so in hot, water. It is easily decomposed by acids. It dyes wool a dull yellow, but has very little affinity for cotton:

Found, N = 11·16; K = 8·26.

$C_{22}H_{23}O_4N_4SK$ requires N = 11·43; K = 7·96 per cent.

Condensation Product with α-Naphthylamine: Phenetoleazosulphobenzylidene-α-naphthylamine, $OEt\cdot C_6H_4\cdot N{:}N\cdot C_6H_3(SO_3H)\cdot CH{:}N\cdot C_{10}H_7$.

The *potassium* salt forms bright orange, silky needles, sparingly soluble in cold, more readily so in hot, water. It dyes wool reddish-yellow shades from a neutral or acetic acid bath, but has no affinity for cotton:

Found, N = 8·51; K = 8·01.

$C_{25}H_{20}O_4N_3SK$ requires N = 8·45; K = 7·85 per cent.

Condensation Product with β-Naphthylamine: Phenetoleazosulphobenzylidene-β-naphthylamine.

The *potassium* salt forms fine orange needles, readily soluble in hot, but sparingly so in cold, water. It dyes wool reddish-yellow shades, but has no affinity for cotton:

Found, N = 8·50; K = 7·96.

$C_{25}H_{20}O_4N_3SK$ requires N = 8·45; K = 7·85 per cent.

Condensation Product with Aminoazobenzene: Phenetoleazosulphobenzylideneaminoazobenzene,

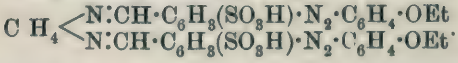
$OEt\cdot C_6H_4\cdot N{:}N\cdot C_6H_3(SO_3H)\cdot CH{:}N\cdot C_6H_4\cdot N{:}N\cdot C_6H_5$.

The *potassium* salt crystallises from dilute alcohol in beautiful, orange, silky needles. It dissolves in hot water to a yellow solution, but is sparingly soluble in the cold solvent. The addition of hydrochloric acid produces a red precipitate of the free acid. It dyes wool from a neutral or acetic acid bath in yellow shades, which are very fast, to alkalis and light. It also has a moderate affinity for cotton, which it dyes from a salt-bath. The affinity for cotton is, however, considerably less than that of chrysophenin, to which it presents some structural analogy:

Found, N = 12·80; K = 6·93.

$C_{27}H_{22}O_4N_5SK$ requires N = 12·70; K = 7·07 per cent.

Condensation Product with p-*Phenylenediamine: Bisphenetoleazosulphobenzylidene-*p-*phenylenediamine,*



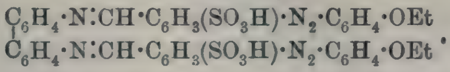
$$C\,H_4<\begin{matrix}N{:}CH\cdot C_6H_3(SO_3H)\cdot N_2\cdot C_6H_4\cdot OEt\\ N{:}CH\cdot C_6H_3(SO_3H)\cdot N_2\cdot C_6H_4\cdot OEt\end{matrix}$$

The *potassium* salt was obtained as a brownish-yellow powder, sparingly soluble in water. It dyes wool in reddish-yellow shades fast to alkalis and light. It also dyes cotton, for which it has a rather greater affinity than the preceding compound:

Found, $N = 9{\cdot}98$; $K = 9{\cdot}52$.

$C_{36}H_{30}O_8N_6S_2K_2$ requires $N = 10{\cdot}29$; $K = 9{\cdot}59$ per cent.

Condensation Product with Benzidine: *Bisphenetoleazosulphobenzylidenebenzidine*,



$$\begin{array}{l} C_6H_4{\cdot}N{:}CH{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_6H_4{\cdot}OEt \\ | \\ C_6H_4{\cdot}N{:}CH{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_6H_4{\cdot}OEt \end{array}$$

The *potassium* salt forms orange needles, moderately soluble in hot, but sparingly so in cold, water. Hydrochloric acid produces a red precipitate. It dyes wool in fast reddish-yellow shades, and also cotton from a salt-bath in yellow shades tolerably fast to soaping:

Found, $N = 9{\cdot}30$; $K = 8{\cdot}99$.

$C_{42}H_{34}O_8N_6S_2K_2$ requires $N = 9{\cdot}42$; $K = 8{\cdot}75$ per cent.

Condensation Product with Hydrazine: *Bisphenetoleazobenzaldazinedisulphonic Acid*,

$OEt{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(SO_3H){\cdot}CH{:}N{\cdot}N{:}CH{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_6H_4{\cdot}OEt$.

This compound was prepared in order to study the tinctorial effect of the double azomethine or aldazine group $\cdot CH{:}N{\cdot}N{:}CH\cdot$. It is obtained by adding 1 gram of hydrazine sulphate dissolved in 20 c.c. of hot water to a solution of 5·7 grams of the aldehyde potassium salt in 300 c.c. of boiling water. The solution, when neutralised with potassium carbonate, deposits the *potassium* salt as a crystalline, yellow precipitate. It crystallises in fine orange needles, sparingly soluble in hot, but almost insoluble in cold, water. Hydrochloric acid produces a red precipitate of the free acid. It dyes wool from a neutral or acetic acid bath in reddish-yellow shades which are fast to alkalis and light. Its affinity for cotton is rather small:

Found, $N = 11{\cdot}22$; $K = 10{\cdot}42$.

$C_{30}H_{26}O_8N_6S_2K_2$ requires $N = 11{\cdot}35$; $K = 10{\cdot}58$ per cent.

DEPARTMENT OF TINCTORIAL CHEMISTRY.
UNIVERSITY OF LEEDS.

CCXXXVI.—*Aromatic Hydroxy-sulphoxides.*

By MAUD GAZDAR and SAMUEL SMILES.

IN the study of the sulphination of certain phenolic ethers (Smiles and Le Rossignol, Trans., 1908, **93**, 745) several thionyl derivatives of these substances were obtained, and it was found that these methoxy- and ethoxy-sulphoxides when dissolved in concentrated sulphuric acid may be converted by excess of phenolic ether into the triarylsulphonium salts. Later investigation of the corresponding hydroxy-derivatives showed that the reaction is not generally applicable to these substances, for, whilst di-*p*-hydroxyphenyl sulphoxide (Smiles and Bain, Trans., 1907, **91**, 1118) yields the trihydroxyphenylsulphonium base, the di-*p*-hydroxy-*m*-tolyl sulphoxide does not (Smiles and Hilditch, Proc., 1907, **23**, 161). The exceptional behaviour of this *p*-cresol sulphoxide is of peculiar interest, for the corresponding dimethyl ether, $(C_6H_3Me{\cdot}OMe)_2SO$, readily furnishes the triarylsulphonium derivative. Although the so-called "steric" conditions which are set up by substitution in the aromatic nucleus are known to be capable of retarding this reaction (Smiles and Le Rossignol, *loc. cit.*), it cannot be supposed that their influence is the cause of the inactivity of this *p*-cresol sulphoxide. For it is evident from previous experience of "steric hindrance" that, if there be any difference in reactivity between a phenol and its ether, it is the latter that should be less reactive, whereas in the present case the reverse relation holds.

It is a remarkable fact that of the eleven hydroxy- or methoxyphenyl sulphoxides which have been hitherto examined, all give brilliantly coloured solutions in concentrated sulphuric acid, and it therefore seemed probable that in effecting the condensation of the sulphoxide with the phenolic ether by means of this reagent, some intermediate compound is formed, and that it is the reactivity of this substance that determines the formation of the sulphonium salt.

As a preliminary step in the investigation, we have found it necessary to extend the range of material available, since very little is known of the aromatic hydroxy-sulphoxides, only one, apparently, having been obtained in a pure condition.

The present paper deals with the sulphoxides of *p*-cresol, *p*-chlorophenol, and *o*-chlorophenol. The investigation is not yet complete, but the results are now published, since one of us is unable to carry on the work.

EXPERIMENTAL.

p-***Cresol***-m-***sulphoxide***, $(OH{\cdot}C_6H_3Me)_2SO$. (Me : OH : SO = 1 : 4 : 3.)

The sulphination of *p*-tolyl methyl ether with sulphurous acid and aluminium chloride yields the sulphoxide and a small quantity of sulphinic acid, the sulphonium base, which is the final product of normal sulphination, being entirely suppressed (Smiles and Le Rossignol, *loc. cit.*). On applying this method to *p*-cresol, similar products were obtained; but the yields of sulphoxide were poor, hence advantage was taken of the stronger sulphinating power of thionyl chloride. Although this reagent is apt to yield sulphonium salts if allowed to act too energetically, we find that by preserving suitable conditions excellent yields of the sulphoxide are obtained.

Fifteen grams of powdered aluminium chloride were dissolved in an ice-cold solution of 20 grams of *p*-cresol in 50 c.c. of carbon disulphide, and then 20 grams of thionyl chloride were gradually added. The mixture was set aside in a desiccator, and, after the lapse of twenty-four hours, the greater portion of the reaction product—evidently a double salt of the sulphoxide with aluminium chloride—had separated in the form of a yellow, viscous mass. During the next twenty-four hours a further small quantity of this product separated; the supernatant layer of carbon disulphide was then decanted, and the residue decomposed with crushed ice. After being mixed with dilute hydrochloric acid, the mass was treated with a current of steam to remove carbon disulphide and unattacked cresol. After this operation, the contents of the flask were cooled, and the hard, granular mass was collected, dried, powdered, and then extracted with a small quantity of benzene, which removed coloured impurities.

The yield of this product, which consisted of the almost pure sulphoxide, was 20 grams, or about 85 per cent. of the theoretical. It was finally crystallised from hot glacial acetic acid, from which it separated in colourless prisms. The pure substance melts and decomposes at 185°:

0·1706 gave 0·3977 CO_2 and 0·0836 H_2O. C = 63·6; H = 5·4.
$C_{14}H_{14}O_3S$ requires C = 64·12; H = 5·34 per cent.

It furnishes a bright blue solution with concentrated sulphuric acid, but does not then condense with phenolic ethers, as do other sulphoxides of this group.

Some derivatives of this sulphoxide have been previously investigated by Mr. Hilditch and one of the present authors (Proc., 1907, **23**, 161), and, together with others since examined, they are now described in detail.

Dibenzoyl-p-*cresol sulphoxide* was obtained from the parent substance by the action of benzoyl chloride in alkaline solution. It is soluble in hot alcohol, and separates from that medium in colourless plates, melting at 173°:

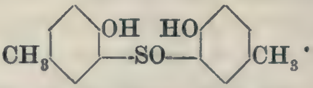
0·1375 gave 0·3591 CO_2 and 0·0593 H_2O. C = 71·23; H = 4·8.
$C_{28}H_{22}O_5S$ requires C = 71·46; H = 4·68 per cent.

Di-p-*cresol Sulphide*, $(OH\cdot C_6H_3Me)_2S$.

The sulphoxide was reduced by the action of zinc dust on the hot solution in glacial acetic acid. On mixing the filtered solution with water, the sulphide separated as a colourless oil, which slowly solidified. After being recrystallised from dilute acetic acid, *di*-p-*cresol sulphide* was obtained in colourless needles, which melted at 143°:

0·1900 gave 0·4735 CO_2 and 0·0984 H_2O. C = 67·97; H = 5·7.
$C_{14}H_{14}O_2S$ requires C = 68·29; H = 5·68 per cent.

Previous experiments have shown that the sulphoxide which is formed (Smiles and Le Rossignol, *loc. cit.*) by the interaction of thionyl chloride and *p*-tolyl methyl ether contains the quadrivalent sulphur group in the ortho-position with respect to methoxyl, and there can be little doubt that the hydroxy-derivative, which is prepared in a similar manner from *p*-cresol, has the same constitution, namely:



Further and independent evidence in support of this structure will be adduced in a subsequent communication, but at present it may be observed that this is borne out by the behaviour of the substance on nitration. It is extremely easily attacked by nitric acid, two nitro-groups being at first inserted; but attempts to induce further nitration by intensifying the conditions of reaction result in the elimination of the thionyl group with formation of dinitrocresol. The most favourable conditions for nitration are as follows:

Nitric acid (2·7 c.c. of D 1·5) is gradually added to a cooled solution of the sulphoxide (5 grams; about two-thirds of the theoretical amount) in glacial acetic acid (100 c.c.). After three to four minutes a large bulk of water is added. The precipitate is collected and boiled with alcohol to remove soluble impurities, and the insoluble residue finally recrystallised.

Nitro-p-*cresol sulphoxide* is soluble in hot glacial acetic acid, and very sparingly so in boiling alcohol; it separates from the latter medium in lemon-yellow prisms, which melt at 214°. The scarlet *sodium* salt is readily soluble in water:

0·1718 gave 0·3009 CO_2 and 0·0545 H_2O. C = 47·7; H = 3·8.
$C_{14}H_{12}O_7N_2S$ requires C = 47·73; H = 3·41 per cent.

Action of Hydrochloric Acid.—Five grams of nitro-*p*-cresol sulphoxide were suspended in about 50 c.c. of alcohol, which had previously been saturated with dry hydrogen chloride at the atmospheric temperature. The mixture was heated to 100° in a sealed tube for four to five hours. Finally, the solid product was collected, washed with alcohol, and then crystallised from hot glacial acetic acid, from which it separated in long, orange needles. The weight of the crude substance was almost equal to that of the sulphoxide employed. When pure it did not contain halogen:

0·1305 gave 0·2382 CO_2 and 0·0410 H_2O. C = 49·78; H = 3·5.
0·1392 „ 0·2532 CO_2 „ 0 0490 H_2O. C = 49·6; H = 3·9.
$C_{14}H_{12}O_6N_2S$ requires C = 50·00; H = 3·5 per cent.

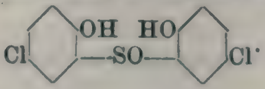
The analytical data and the properties of the substance show that it is *nitro*-p-*cresol sulphide*. This compound melts at 194°, and is soluble in hot alcohol and insoluble in water; the *sodium* salt is deep red in colour. Other sulphoxides, which are described in the following pages, have been treated in a similar manner, and similar reactions have been observed; but with less highly substituted aromatic nuclei chlorination occurs, and even elimination of the sulphur may take place. It may be recalled that other oxygen derivatives of quadrivalent sulphur, namely, the sulphinic acids, are similarly reduced by mineral acids.

p-*Chlorophenol Sulphoxide.*

The sulphination of *p*-chlorophenol was effected with thionyl chloride under conditions similar to those described in the preparation of the *p*-cresol derivative. The crude product, which was obtained in a yield of about 70 per cent. of the theoretical, was purified by precipitation with dilute hydrochloric acid from an alcoholic solution. The substance was finally crystallised from dilute alcohol, from which it separated in small, colourless prisms. It melts at 202°, and is sparingly soluble in ether or hot water, and readily so in cold alcohol:

0·1487 gave 0·2580 CO_2 and 0·0366 H_2O. C = 47·33; H = 2·73.
0·3538 „ 0·331 AgCl „ 0·2780 $BaSO_4$. Cl = 23·2; S = 10·8.
$C_{12}H_8O_3Cl_2S$ requires C = 47·52; H = 2·73; Cl = 23·43;
S = 10·56 per cent.

p-*Chlorophenol sulphoxide* is soluble in concentrated sulphuric acid, the solution being at first colourless, but rapidly assuming a bright blue colour, which is slowly discharged by the addition of phenetole, indicating the formation of a sulphonium salt. Is will be shown in a subsequent communication that the thionyl group in this sulphoxide occupies the ortho-position with respect to the two hydroxyl groups of the phenolic nuclei, the substance having the structure:



p-*Chloronitrophenol Sulphoxide.*

When submitted to the action of nitric acid, this chloro-sulphoxide behaves like the similarly constituted *p*-cresol sulphoxide; two nitro-groups are readily absorbed, but further action of the acid results in decomposition. The dinitro-derivative was prepared in the following manner. The sulphoxide was suspended in about thirty times its weight of cold glacial acetic acid, and while the mixture was stirred, exactly the calculated amount of nitric acid (D 1·42) was added. Stirring was continued until almost all the finely-divided solid had dissolved, then the mixture was rapidly filtered, and the dark reddish-brown filtrates were immediately poured into a large bulk of water. The precipitate was collected and extracted with alcohol; finally, the insoluble portion was recrystallised in small quantities from hot glacial acetic acid. In this way, p-*chloronitrophenol sulphoxide* is obtained in fine yellow needles, which melt at 180—181°. It is insoluble in cold water and sparingly soluble in boiling alcohol:

0·1740 gave 0·2342 CO_2 and 0·0341 H_2O. C = 36·7; H = 2·1.

$C_{12}H_6O_7N_2Cl_2S$ requires C = 36·64; H = 1·53 per cent.

p-*Chlorophenol Sulphide.*

The sulphide may be obtained by the action of hydrochloric acid on the sulphoxide in alcoholic solution under conditions similar to those described in the preparation of the nitrocresol derivative. To isolate the substance, the mixture was poured into water, and, after some hours had elapsed, the solid was collected and recrystallised several times from benzene, when it was obtained in colourless leaflets which melted at 173—174°. It was found difficult completely to purify this substance, since it tenaciously retained sulphides of higher chlorine content. For comparison, the sulphide was prepared by the reduction of the sulphoxide in the usual manner with zinc dust and boiling acetic acid, and the product, after recrystallisation from benzene, melted sharply at 174° and contained the requisite amount of halogen:

0·1280 gave 0·1288 AgCl. Cl = 24·79.

$C_{12}H_8O_2Cl_2S$ requires Cl = 24·71 per cent.

When mixed with this substance, the product obtained by the former method retained the same melting point.

o-*Chlorophenol Sulphoxide.*

Sulphination of *o*-chlorophenol was conducted as with *p*-cresol and *p*-chlorophenol; the yield of crude sulphoxide was approximately the same as that recorded in these cases. The coloured impurities were removed by trituration with cold glacial acetic acid, then the insoluble material was collected, and finally purified by recrystallisation from dilute alcohol, to which a little hydrochloric acid had been added. *o-Chlorophenol sulphoxide* forms fine colourless needles, which melt at 195°, and are soluble in most hot organic media:

0·1504 gave 0·2600 CO_2 and 0·0383 H_2O. $C = 47·21$; $H = 2·83$.
0·1535 „ 0·1415 AgCl. $Cl = 22·8$.
0·2032 „ 0·1485 $BaSO_4$. $S = 10·0$.
$C_{12}H_8O_3Cl_2S$ requires $C = 47·52$; $H = 2·73$; $Cl = 23·4$; $S = 10·5$ per cent.

The substance dissolves in concentrated sulphuric acid, forming a blue solution, from which the colour is removed by the addition of a phenolic ether, a sulphonium base being then formed. The action of alcoholic hydrogen chloride on this substance is somewhat different from that observed in the preceding cases. After the usual treatment, the reaction mixture was submitted to distillation in a current of steam. The white, crystalline solid which separated from the distillate was evidently dichlorophenol, for it melted at 43° and contained 43·4 per cent. of chlorine (calc., $Cl = 43·55$ per cent.). The non-volatile portion consisted of an oil which resisted all attempts at purification; it apparently consisted of a mixture of polychloro-sulphides.

In conclusion, we desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed the expenses of these experiments.

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CCXXXVII.—*Some Phenolic Derivatives of β-Phenylethylamine.*

By GEORGE BARGER AND ARTHUR JAMES EWINS.

p-HYDROXY-β-PHENYLETHYLAMINE, $OH·C_6H_4·CH_2·CH_2·NH_2$, which is formed by the action of micro-organisms from tyrosine and from proteins containing tyrosine, has been shown to have a pronounced physiological activity (Barger and Walpole, *J. Physiol.*, 1909, **38**, 343); it is, for instance, one of the active constituents of ergot extracts (Barger, Trans., 1909, **95**, 1123).

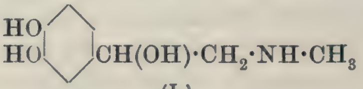
Since the effect of this base on the vascular system and on certain organs is essentially similar to that of adrenaline (Dale and Dixon, *J.*

Physiol., 1909, **39**, 25), to which *p*-hydroxy-β-phenylethylamine is also chemically related, an examination of a considerable number of similarly constituted amines was undertaken by Dale in order to trace as far as possible the connexion between physiological activity and chemical structure within the limits of this group (Barger and Dale, *J. Physiol.*, 1910, **41**, 19).

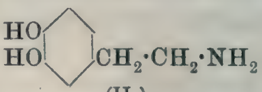
The present paper deals with the synthesis of some of these amines. They were chosen for the following reasons:

(1) Since the bactericidal action of phenol is greatly enhanced by the introduction of a methyl group into the benzene ring (yielding cresol), we prepared 3-methyl-4-hydroxy-β-phenylethylamine. The pressor action of this base was found, however, to be only about one half as great as that of the parent substance.

(2) One of the differences between *p*-hydroxy-β-phenylethylamine and adrenaline (I) is that the former substance has only a single phenolic hydroxyl group as compared with two in the latter substance.



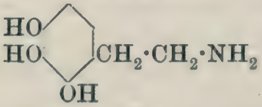
(I.)



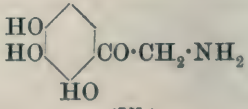
(II.)

We therefore prepared 3:4-dihydroxy-β-phenylethylamine (II), which was found to be scarcely more active than the monophenolic amine although its *N*-methyl derivative, obtained by Pyman from an oxidation product of laudanosine (this vol., p. 268), approximates much more closely to adrenaline.

(3) Since in several cases the introduction of a second phenolic hydroxyl group greatly increases the physiological activity of bases of this type, we wished to trace the effect of introducing yet another phenolic hydroxyl group, and for this purpose prepared 2:3:4-*trihydroxy-β-phenylethylamine* (III) and *ω-aminogallacetophenone* (IV).



(III.)



(IV.)

Both these bases were somewhat less active than the corresponding dihydroxy-bases (namely, 3:4-dihydroxy-β-phenylethylamine and ω-aminoacetylcatechol).

The close chemical relationship of the bases (I), (II), (III), and (IV) is further illustrated by the fact that they all give the colour reactions hitherto described as characteristic for adrenaline (I) (Ewins, *J. Physiol*, 1910, **40**, 317).

The synthesis of 4-*hydroxy-β*-m-*tolylethylamine* started with *m*-tolylacetonitrile, and was completely analogous to that of *p*-hydroxy-β-phenylethylamine from phenylacetonitrile (Barger, Trans., 1909, **95**, 1123).

3 : 4-Dihydroxy-β-phenylethylamine was obtained from its dimethyl ether, and has already been described by Mannich (*Ber.*, 1910, **43**, 196).

The production of the pyrogallol bases (III and IV) at first gave considerable difficulty. The 2 : 3 : 4-trihydroxybenzaldehyde required for (III) had to be prepared with anhydrous hydrogen cyanide according to Gattermann's method. It was found impossible to obtain 2 : 3 : 4-trimethoxy-β-phenylethylamine from 2 : 3 : 4-trimethoxyphenylpropionamide by Hofmann's reaction, although this method was employed in preparing the corresponding dimethoxy-base. We therefore had to use Curtius's method, starting from 2 : 3 : 4-trimethoxyphenylpropionylhydrazide.

In the case of ω-aminogallacetophenone (IV) we found it quite impossible to isolate a pure substance when ω-chlorogallacetophenone was acted on by ammonia, although this method is employed technically in the case of ω-chloroacetylcatechol; the substance is destroyed too readily in alkaline solution. We therefore had recourse to an indirect method; ω-chlorogallacetophenone reacts readily with sodium azide, and from the *ω-triazogallacetophenone*, $C_6H_2(OH)_3{\cdot}CO{\cdot}CH_2{\cdot}N_3$, thus produced the required amine is obtainable by reduction.

In the course of our work on this subject we have also prepared β-phenylethylmethylamine, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_3$, of which adrenaline is the trihydroxy-derivative. Two methods for preparing this base will be mentioned, although it is not a phenolic amine, and was recently prepared by Johnson and Guest (*Amer. Chem. J.*, 1909, **42**, 340) according to a third method (methylation of benzenesulphonylphenylethylamine and subsequent hydrolysis).

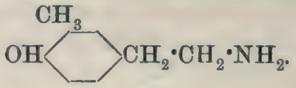
EXPERIMENTAL.

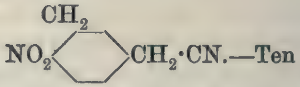
β-Phenylethylmethylamine, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_3$.

As the direct methylation of β-phenylethylamine yields a quaternary iodide, we condensed methylamine (in 33 per cent. aqueous solution) with phenylacetaldehyde by means of sodium hydroxide, and reduced the crude condensation product, which separated out, with sodium and alcohol. The base was isolated as the oxalate.

A second, and more convenient, method consists in acting on α-chloro-β-phenylethane, $C_6H_5{\cdot}CH_2{\cdot}CH_2Cl$ (Barger, Trans, 1909, **95**, 2194), with an excess of a 33 per cent. alcoholic solution of methylamine at 100° for several hours. The base thus obtained was distilled (b. p. 205°), and its hydrochloride was analysed. (Found, Cl = 20·7. Calc., Cl = 20·4 per cent.)

Preparation of 4-*Hydroxy-β-*m-*tolylethylamine,*



p-*Nitro*-m-*tolylacetonitrile,*  —Ten grams of *m*-tolylacetonitrile (Seńkowski, *Monatsh.*, 1888, **9**, 854) were dropped into 40 c.c. of nitric acid (D 1·5) at a temperature below −5°. The acid solution was then poured into water and extracted with ether. After washing with sodium carbonate, drying, and distilling, a fraction boiling at 201—205°/22 mm. was collected, which solidified, and on crystallisation from ether and light petroleum melted at 52°. The yield was 80 per cent. of the theoretical:

0·1584 gave 0·3554 CO_2 and 0·0665 H_2O. C = 61·2; H = 4·6.
$C_9H_8O_2N_2$ requires C = 61·4; H = 4·5 per cent.

p-*Amino*-m-*tolylacetonitrile,* $NH_2·C_6H_3Me·CH_2·CN$.—*p*-Nitro-*m*-tolylacetonitrile (19 grams) was dissolved in alcohol (240 c.c.), tin-foil (25 grams), and then gradually concentrated hydrochloric acid (120 c.c.) was added. The temperature was at first kept below 60°, finally being raised to 100°. After extraction with ether, the base was distilled, and 8·5 grams (60 per cent.) boiling at 175—185°/20 mm. were obtained. On crystallisation from benzene, the substance melted at 87°:

0·1552 gave 0·4204 CO_2 and 0·0902 H_2O. C = 73·9; H = 6·5.
$C_9H_{10}N_2$ requires C = 74·0; H = 6·8 per cent.

The *hydrochloride*, prepared by adding alcoholic hydrogen chloride to the ethereal solution of the base, melts at 247—248°:

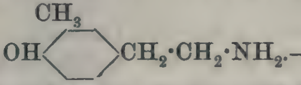
0·2082 gave 0·1620 AgCl. Cl = 19·3.
$C_9H_{10}N_2,HCl$ requires Cl = 19·4 per cent.

The *oxalate* melts at 164—165°:

0·1884 gave 24 c.c. N_2 (moist) at 20° and 768 mm. N = 14·7.
$(C_9H_{10}N_2)_2,H_2C_2O_4$ requires N = 14·7 per cent.

p-*Hydroxy*-m-*tolylacetonitrile,* $OH·C_6H_3Me·CH_2·CN$.—3·9 Grams of sodium nitrite dissolved in a little water were slowly added to a boiling solution of 8·5 grams of the amino-compound dissolved in 200 c.c. of dilute sulphuric acid (210 c.c. of water and 17 c.c. of concentrated sulphuric acid). On extracting the acid solution with ether, 2·5 grams (30 per cent.) of a substance were obtained, which distilled at 162—164°/2 mm. and crystallised in the receiver. It crystallises from benzene in leaflets melting at 84°:

0·1526 gave 0·4093 CO_2 and 0·0807 H_2O. C = 73·1 ; H = 5·9.
0·1718 „ 14·2 c.c. N_2 (moist) at 22° and 760 mm. N = 9·4.
C_9H_9ON requires C = 73·5 ; H = 6·1 ; N = 9·5 per cent.

4-*Hydroxy-β-*m-*tolylethylamine*, 

.—0·9 Gram of *p*-hydroxy-*m*-tolylacetonitrile yielded, on reduction with 4 grams of sodium in boiling alcoholic solution, 0·62 gram of a crude hydrochloride, which was crystallised by adding ether to its concentrated solution in alcohol. From this the free base was obtained ; it crystallised from xylene, and, after sublimation in a vacuum, melted at 132—133° :

0·1290 gave 0·3364 CO_2 and 0·0910 H_2O. C = 71·2 ; H = 7·9.
$C_9H_{13}ON$ requires C = 71·5 ; H = 8·6 per cent.

The *hydrochloride* was also analysed :

0·1226 gave 0·0956 AgCl. Cl = 19·3.
$C_9H_{13}ON,HCl$ requires Cl = 19·0 per cent.

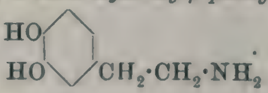
The *dibenzoyl* derivative crystallised from dilute alcohol in long, thin needles, melting at 130—131°.

The *quaternary iodide*, $OH{\cdot}C_6H_3Me{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3I$, was obtained by boiling the base with a little methyl alcohol and a large excess of methyl iodide. It melts at 231—232°, and closely resembles hordenine methiodide in solubility and other properties.

4-Hydroxy-*β*-*m*-tolylethylamine resembles *p*-hydroxy-*β*-phenylethylamine in behaviour and derivatives.

The physiological action of the former base is about one-half of the latter. Both bases give Millon's reaction, but it is significant that, unlike *p*-hydroxy-*β*-phenylethylamine, the tolyl compound does not give Mörner's reaction (green coloration after heating with sulphuric acid and formaldehyde). It would appear that substitution in the phenolic ring prevents this reaction from taking place.

Preparation of 3 : 4-*Dihydroxy-β-phenylethylamine,*



3 : 4-Dimethoxy-*β*-phenylethylamine was prepared from vanillin according to the method described in detail by Pictet and Finkelstein (*Ber.*, 1909, **42**, 1979), and 5·2 grams of the amine boiling at 164—166°/13 mm. were obtained from 20·5 grams of homoveratric acid.

The amine was hydrolysed by heating with ten parts of concentrated hydrochloric acid to 170° for two hours. The hydrochloride so obtained crystallised from 90 per cent. alcohol in glistening, almost colourless plates, melting and decomposing at 240—241°. Yield, 45 per cent. of the theoretical. (Found, C = 50·6 ; H = 6·2. Calc., C = 50·7 ; H = 6·2 per cent.

The *hydrobromide* was obtained by heating the dimethoxy-amine to 130° for two hours with ten times its weight of concentrated aqueous hydrobromic acid. The crystalline hydrobromide was obtained quite pure in the same manner as that employed in the preparation of the hydrochloride. The salt crystallises in plates, melting at 212° :

0·1212 gave 0·0984 AgBr. Br = 34·5.

$C_8H_{12}O_2NBr$ requires Br = 34·2 per cent.

The aqueous solution of the salts of 3 : 4-dihydroxy-β-phenylethylamine gave an intense green coloration with ferric chloride.

The quaternary chloride, $C_6H_3(OH)_2\cdot CH_2\cdot CH_2\cdot NMe_3Cl$, was prepared in order to compare its action with that of hordenine methiodide, $OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NMe_3I$. The action of the two substances is very similar, like that of nicotine, and unlike that of adrenaline.

3 : 4-*Dihydroxy-β-phenylethyltrimethylammonium chloride* was obtained from 3 : 4-dimethoxy-β-phenylethylamine. The quaternary iodide obtained by treating the latter base with methyl iodide was transformed into the chloride by digestion with silver chloride, and was then hydrolysed by concentrated hydrochloric acid at 170°. On removal of the latter, the residue crystallised from alcohol and ether, and melted at 201°.

Preparation of 2 : 3 : 4-*Trihydroxy-β-phenylethylamine*, $C_6H_2(OH)_3\cdot CH_2\cdot CH_2\cdot NH_2$.

2 : 3 : 4-*Trimethoxybenzaldehyde*, $C_6H_2(OMe)_3\cdot CHO$.—This aldehyde does not appear to have been described before, although F. Mauthner (*Ber.*, 1909, **42**, 188) has stated that it can be obtained from 2 : 3 : 4-trimethoxyphenylglyoxylic acid by the action of aniline. The methylation of 2 : 3 : 4-trihydroxybenzaldehyde, which was prepared from pyrogallol and anhydrous hydrocyanic acid according to Gattermann and Kœbner's method (*Ber.*, 1899, **32**, 281), was carried out in an atmosphere of hydrogen by the method employed by Perkin and Robinson (Trans., 1907, **91**, 1079) for the preparation of veratraldehyde from vanillin. Twenty-five grams of 2 : 3 : 4-trihydroxybenzaldehyde were dissolved in 80 c.c. of methyl alcohol, and to this solution was added 24 grams of sodium hydroxide dissolved in the minimum quantity of water. The solution became very dark brown in colour. Eighty grams of methyl sulphate were then added, and when the vigorous reaction had nearly subsided, a further 66 grams in small quantities alternately with small quantities of sodium hydroxide were added at such a rate that a vigorous reaction was maintained.

The mixture was kept for half an hour, and then poured into 500 c.c. of water. An oil separated, which was extracted by means of ether, and, after drying and removal of the solvent, the residue was distilled. 18·5 Grams of a colourless liquid, boiling at 168—170°/12 mm., were thus obtained. The distillate solidified after some time to a crystalline mass of long, thin needles, melting at 30°:

0·1840 gave 0·4126 CO_2 and 0·1020 H_2O. C = 61·1 ; H = 6·2.

$C_{10}H_{12}O_4$ requires C = 61·2 ; H = 6·1 per cent.

2 : 3 : 4-*Trimethoxy-β-phenylpropionic Acid*, $C_6H_2(OMe)_3 \cdot CH_2 \cdot CH_2 \cdot CO_2H$.

Twenty grams of 2 : 3 : 4-trimethoxybenzaldehyde were dissolved in 35 grams of ethyl acetate, and the solution added to 3·3 grams of finely divided sodium contained in a large flask provided with a reflux condenser. A vigorous reaction ensued. The product was kept for one hour, and then a solution of 14 grams of sodium hydroxide in methyl alcohol was added. After the reaction had ceased, 250 c.c. of water were added. The alcohol was then removed by evaporation on a water-bath, water being added from time to time to avoid undue concentration. The alkaline solution was then reduced by the addition of 500 grams of 2½ per cent. sodium amalgam in small portions, concentrated hydrochloric acid being added from time to time to neutralise the excess of sodium hydroxide formed in the reaction. The resulting solution was filtered, and acidified with hydrochloric acid. A yellow oil separated, which slowly crystallised. The acid was purified by distillation under diminished pressure (it boils at 200—203°/2 mm.) and subsequent crystallisation from ether and light petroleum, from which it separated in clusters of prisms, melting at 76°. Yield, 50 per cent. of the theoretical:

0·2150 gave 0·4722 CO_2 and 0·1282 H_2O. C = 59·9 ; H = 6·6.

$C_{12}H_{16}O_5$ requires C = 60·0 ; H = 6·7 per cent.

Ethyl 2 : 3 : 4-*Trimethoxy-β-phenylpropionate*, $C_6H_2(OMe)_3 \cdot CH_2 \cdot CH_2 \cdot CO_2Et$.

The acid obtained as above was converted into the corresponding ethyl ester by dissolving in five times its weight of 5 per cent. alcoholic hydrogen chloride and boiling under reflux for six hours. The alcohol and hydrochloric acid were evaporated off, and the residue was distilled. The ester boils at 200—201°/20 mm. Yield, 70 per cent. of the theoretical:

0·2074 gave 0·4797 CO_2 and 0·1390 H_2O. C = 63·1 ; H = 7·4.

$C_{14}H_{20}O_5$ requires C = 62·7 ; H = 7·4 per cent.

2 : 3 : 4-*Trimethoxy-β-phenylpropionylhydrazide Hydrochloride,*

$C_6H_2(OMe)_3\cdot CH_2\cdot CH_2\cdot CO\cdot NH\cdot NH_2,HCl$.

Two grams of the above ester were gradually added to 0·6 gram of boiling hydrazine hydrate. Solution was complete at the end of one hour, and the solution was boiled under reflux for several hours longer. The excess of hydrazine was removed by evaporation in a vacuum over sulphuric acid. The syrupy residue could not be crystallised, but on dissolving in alcohol and adding a little alcoholic hydrogen chloride a crystalline precipitate separated, which was increased by the addition of ether. The hydrochloride thus obtained was recrystallised from 98 per cent. alcohol, separating in the form of hexagonal plates, which melted at 155°:

0·1679 gave 0·3020 CO_2 and 0·0947 H_2O. C = 49·0 ; H = 6·3.

$C_{12}H_{19}O_4N_2Cl$ requires C = 48·8 ; H = 6·5 per cent.

The solution of this salt readily reduced ammoniacal silver in the cold, and Fehling's solution on boiling.

2 : 3 : 4-*Trihydroxy-β-phenylethylamine Hydrochloride,*

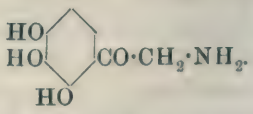
$C_6H_2(OH)_3\cdot CH_2\cdot CH_2\cdot NH_2,HCl$.

The hydrazide obtained as described above was diazotised at 0°. The crude azide, obtained by extraction with ether, was converted into the corresponding urethane derivative by boiling in absolute alcoholic solution for twelve hours under reflux. The alcohol was then distilled off, and the residue hydrolysed by heating in a sealed tube with concentrated hydrochloric acid to 170—180° for three hours. The very dark-coloured contents of the tube were evaporated to dryness, dissolved in a little water, boiled with animal charcoal, filtered, and the solution evaporated nearly to dryness. From the dark brown syrupy product, crystals slowly separated. These were pressed on a plate, and recrystallised from absolute alcohol by addition of ether. The crystals, which melted at 162—163°, were still dark brown in colour. The aqueous solution gives with ferric chloride a deep purple-brown coloration, which rapidly fades:

0·1000 gave 0·0700 AgCl. Cl = 17·32.

$C_8H_{11}O_3NCl$ requires Cl = 17·35 per cent.

Preparation of ω-Aminogallacetophenone,



ω-Triazogallacetophenone, $C_6H_2(OH)_3\cdot CO\cdot CH_2\cdot N_3$.—Seven grams of ω-chlorogallacetophenone, prepared according to Nencki's method

(*J. Russ. Phys. Chem. Soc.*, 1883, **25**, 182), were dissolved in 50 c.c. of hot water, and a hot solution of 2·5 grams of sodium azide in a little water added. On cooling, a crystalline solid separated. This was collected and recrystallised from xylene, when rhomb-shaped plates, melting at 155°, were obtained. Yield, 50 per cent. of the theoretical:

0·2460 gave 44·2 c.c. N_2 (moist) at 19° and 758 mm. N = 20·7.

$C_8H_7O_4N_3$ requires N = 20·1 per cent.

ω-Aminogallacetophenone Hydrochloride,

$C_6H_2(OH)_3\cdot CO\cdot CH_2\cdot NH_2,HCl$.

—Five grams of ω-triazogallacetophenone were dissolved in absolute alcohol. Ten grams of tin-foil were then placed in the liquid, and 60 c.c. of concentrated hydrochloric acid added in small portions. As reduction proceeded, the hydrochloride of the base separated out in small, rectangular plates. The yield was 1·2 grams, or 25 per cent. of the theoretical

For analysis, the salt was recrystallised from alcohol and ether, when it melted at 259—260°:

0·1916 gave 10·8 c.c. N_2 (moist) at 17° and 754 mm.
0·1275 „ 0·0838 AgCl. Cl = 16·2; N = 6·5.

$C_8H_{10}O_4NCl$ requires N = 6·4; Cl = 16·1 per cent.

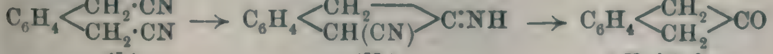
The salt is readily soluble in water; it aqueous solution darkens on keeping, and with very dilute ferric chloride solution gives a dirty green coloration, which rapidly changes to a brownish-yellow.

The Wellcome Physiological Research Laboratories,
Herne Hill, S.E.

CCXXXVIII.—*The Formation and Reactions of Imino-compounds. Part XIV. The Formation of α-Hydrindone and its Derivatives.*

By Alec Duncan Mitchell and Jocelyn Field Thorpe.

Some time ago (Trans., 1908, **93**, 165) it was shown that β-hydrindone and some of its derivatives could be derived from β-imino-α-cyanohydrindene (II), a substance which is formed in quantitative yield when an alcoholic solution of *o*-phenylenediacetonitrile (I), containing a trace of sodium ethoxide, is warmed.

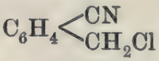


$$C_6H_4{<}\begin{matrix}CH_2\cdot CN\\CH_2\cdot CN\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CH_2\text{———}\\CH(CN)\end{matrix}{>}C{:}NH \longrightarrow C_6H_4{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}CO$$

(I.) (II.) β-Hydrindone.

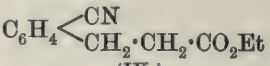
The present paper deals with a similar reaction by which α-hydrindone and its derivatives can be produced through the imino-compound.

α-Hydrindone was originally prepared by Gabriel and Hausmann (*Ber.*, 1889, **22**, 2018), and was subsequently investigated by Hausmann (*ibid.*, p. 2020). Gabriel and Hausmann prepared the ketone by condensing *o*-cyanobenzyl chloride (III) with the sodium compound of ethyl acetoacetate, when a compound, which they considered to be ethyl *o*-cyano-β-phenylpropionate (IV), was formed, and this substance, on treatment with concentrated hydrochloric acid, passed into α-hydrindone (V).



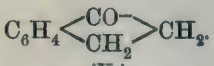
$C_6H_4<\begin{matrix}CN\\CH_2Cl\end{matrix}$

(III.)



$C_6H_4<\begin{matrix}CN\\CH_2\cdot CH_2\cdot CO_2Et\end{matrix}$

(IV.)

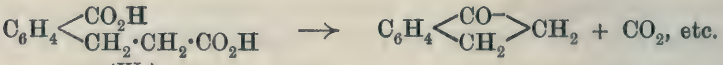


$C_6H_4<\begin{matrix}CO-\\CH_2\end{matrix}>CH_2.$

(V.)

Hausmann (*loc. cit.*) subsequently found that when ethyl sodiomalonate was used in this reaction in place of ethyl sodioacetoacetate, the same substance (IV) was produced.

The formation of α-hydrindone from ethyl *o*-cyano-β-phenylpropionate on treatment with concentrated hydrochloric acid was explained on the assumption that *o*-carboxy-β-phenylpropionic acid (VI) is first formed, which then decomposes into water, carbon dioxide, and α-hydrindone, thus:



$$C_6H_4<\begin{matrix}CO_2H\\CH_2\cdot CH_2\cdot CO_2H\end{matrix} \longrightarrow C_6H_4<\begin{matrix}CO-\\CH_2\end{matrix}>CH_2 + CO_2, \text{ etc.}$$

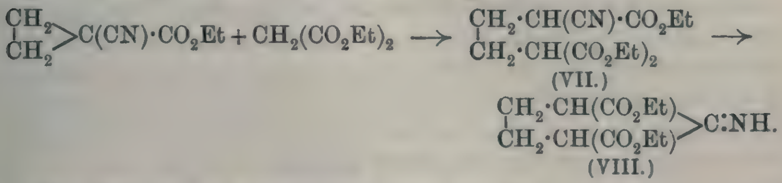
(VI.)

This is also the explanation advanced by Aschan (*Chemie der Alicyklischen Verbindungen*, p. 1028), who remarks that König has shown (*Annalen*, 1893, **275**, 341) that *o*-carboxy-β-phenylpropionic acid passes on distillation into α-hydrindone. It must be remembered, however, that the production of α-hydrindone from *o*-carboxy-β-phenylpropionic acid in this manner takes place at a high temperature, that is to say, under conditions very different from those which convert ethyl *o*-cyano-β-phenylpropionate into this ketone. It therefore seemed to us unlikely that the mechanism of this reaction, as recorded above, could be correct, and we consequently decided to seek for some other explanation more in accordance with the experimental facts.

It has been already mentioned that, according to the observation of Hausmann, the condensation of *o*-cyanobenzyl chloride with both ethyl sodiomalonate and ethyl sodioacetoacetate yields the same product, namely, ethyl *o*-cyano-β-phenylpropionate (IV). It is evident, therefore, that in the first condensation a carbethoxyl group, and in the second condensation an acetyl group, must have been eliminated during the process of the condensation.

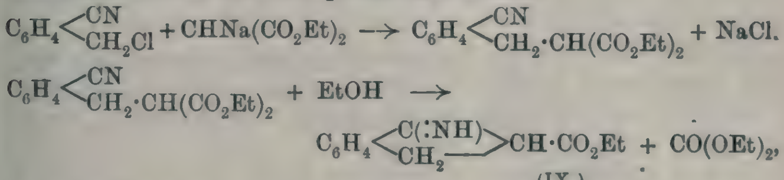
Neither Gabriel nor Hausmann seems to have remarked on this, but, in the light of recent investigation on the formation of five-ring imino-compounds, the fact possessed for us some significance.

Thus we have always found that when the five-carbon ring is formed through the imino-group, the formula of the product does not allow of two carbethoxyl groups, a nitrile group and a carbethoxyl group, or an acetyl group and a carbethoxyl group, being attached to the same carbon atom; an example of this, which bears closely on the present instance, being the transformation of the open-chain compound (VII), which is formed by the condensation of ethyl sodiomalonate and ethyl 1-cyano-*cyclo*propane-1-carboxylate into ethyl 2-imino*cyclo*pentane-1 : 3-dicarboxylate (VIII) (this vol., p. 1002).



$$\left.\begin{matrix}CH_2\\ CH_2\end{matrix}\right>C(CN)\cdot CO_2Et + CH_2(CO_2Et)_2 \longrightarrow \underset{\text{(VII.)}}{\begin{matrix}CH_2\cdot CH(CN)\cdot CO_2Et\\ CH_2\cdot CH(CO_2Et)_2\end{matrix}} \longrightarrow \underset{\text{(VIII.)}}{\left.\begin{matrix}CH_2\cdot CH(CO_2Et)\\ CH_2\cdot CH(CO_2Et)\end{matrix}\right>C{:}NH.}$$

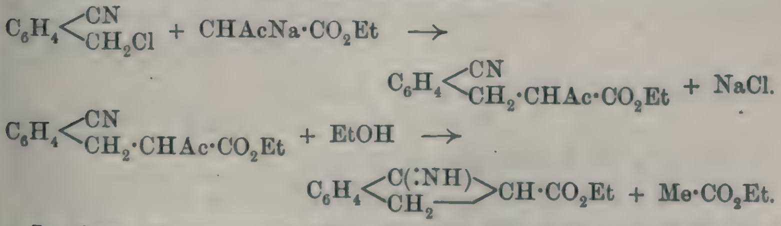
The elimination of a carbethoxy-group in Hausmann's condensation suggested therefore the closing of the five-carbon ring, in which case the reaction would have proceeded as follows:



$$C_6H_4\left<\begin{matrix}CN\\ CH_2Cl\end{matrix}\right. + CHNa(CO_2Et)_2 \longrightarrow C_6H_4\left<\begin{matrix}CN\\ CH_2\cdot CH(CO_2Et)_2\end{matrix}\right. + NaCl.$$

$$C_6H_4\left<\begin{matrix}CN\\ CH_2\cdot CH(CO_2Et)_2\end{matrix}\right. + EtOH \longrightarrow \underset{\text{(IX.)}}{C_6H_4\left<\begin{matrix}C({:}NH)\\ CH_2\end{matrix}\right>CH\cdot CO_2Et} + CO(OEt)_2,$$

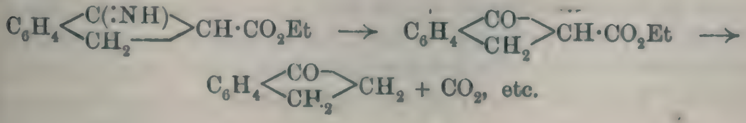
or in the case of ethyl sodioacetoacetate as follows:



$$C_6H_4\left<\begin{matrix}CN\\ CH_2Cl\end{matrix}\right. + CHAcNa\cdot CO_2Et \longrightarrow C_6H_4\left<\begin{matrix}CN\\ CH_2\cdot CHAc\cdot CO_2Et\end{matrix}\right. + NaCl.$$

$$C_6H_4\left<\begin{matrix}CN\\ CH_2\cdot CHAc\cdot CO_2Et\end{matrix}\right. + EtOH \longrightarrow C_6H_4\left<\begin{matrix}C({:}NH)\\ CH_2\end{matrix}\right>CH\cdot CO_2Et + Me\cdot CO_2Et.$$

In these circumstances the compound described by Gabriel and Hausmann as ethyl *o*-cyano-β-phenylpropionate would be ethyl 1-iminohydrindene-2-carboxylate (IX), and its transformation into α-hydrindone by the action of concentrated hydrochloric acid could be readily explained thus:



$$C_6H_4\left<\begin{matrix}C({:}NH)\\ CH_2\end{matrix}\right>CH\cdot CO_2Et \longrightarrow C_6H_4\left<\begin{matrix}CO\\ CH_2\end{matrix}\right>CH\cdot CO_2Et \longrightarrow C_6H_4\left<\begin{matrix}CO\\ CH_2\end{matrix}\right>CH_2 + CO_2, \text{ etc.}$$

Investigation proved that this view of the formation of α-hydrindone was correct, and that the compound described as ethyl *o*-cyano-β-phenylpropionate behaved in every way as an imino-compound of formula (IX). Before this fact could be definitely proved it was necessary, however, to thoroughly study the condensation of *o*-cyanobenzyl chloride with the sodium compounds of both ethyl malonate and ethyl acetoacetate, and as, at the same time, it was thought advisable, for reasons given later, to investigate the corresponding condensation with ethyl sodiocyanoacetate, it is best, for the sake of comparison, to describe the three condensations separately.

(1) *The Condensation of* o-*Cyanobenzyl Chloride with the Sodium Compound of Ethyl Malonate.*—In effecting this condensation, Hausmann used equivalent quantities of sodium dissolved in alcohol, and of the two reacting substances. He found that, mixed with the chief product of the condensation (the so-called ethyl *o*-cyano-β-phenylpropionate), a considerable quantity of a product melting at 86° was also formed. This he showed to be ethyl di-*o*-cyanobenzylmalonate (X),

$$(CN\cdot C_6H_4\cdot CH_2)_2C(CO_2Et)_2,$$

(X.)

which had been formed by the condensation of two molecules of *o*-cyanobenzyl chloride with one molecule of ethyl malonate.

Hausmann separated the two products by treating the mixture with cold concentrated hydrochloric acid, in which the supposed ethyl *o*-cyano-β-phenylpropionate dissolved, and could be obtained on mixing the hydrochloric acid filtrate with water.

Now it is obvious that the formation of the derivative (X) must have taken place in the following manner :

(1) $CN\cdot C_6H_4\cdot CH_2Cl + CHNa(CO_2Et)_2 \longrightarrow CN\cdot C_6H_4\cdot CH_2\cdot CH(CO_2Et)_2 + NaCl.$

(2) $CN\cdot C_6H_4\cdot CH_2\cdot CH(CO_2Et)_2 + CHNa(CO_2Et)_2 \longrightarrow CN\cdot C_6H_4\cdot CH_2\cdot CNa(CO_2Et)_2 + CH_2(CO_2Et)_2.$

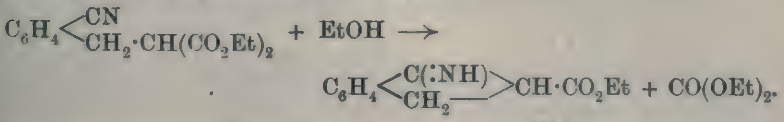
(3) $CN\cdot C_6H_4\cdot CH_2\cdot CNa(CO_2Et)_2 + CN\cdot C_6H_4\cdot CH_2Cl \longrightarrow (CN\cdot C_6H_4\cdot CH_2)_2C(CO_2Et)_2 + NaCl.$

That is to say, the initial condensation product of *o*-cyanobenzyl chloride and ethyl sodiomalonate must be the normal product of the formula $CN\cdot C_6H_4\cdot CH_2\cdot CH(CO_2Et)_2$, and the elimination of a carbethoxyl group must therefore have taken place subsequent to its formation.

Our previous experiments on this point show that the elimination of this group is always effected by the action of free sodium ethoxide, or of some sodium derivative dissociating in alcoholic solution, and hence it seemed to us likely that by preventing, so far as possible, the presence of excess of the sodium derivative of ethyl malonate during the process of the condensation the elimination of this group might be avoided.

This proved to be the case, for it was found that when an alcoholic solution of ethyl sodiomalonate containing a slight excess of ethyl malonate was added slowly to a hot alcoholic solution of *o*-cyanobenzyl chloride, the product of the reaction did not become solid on being poured into water, but remained as a heavy oil at the bottom of the liquid.

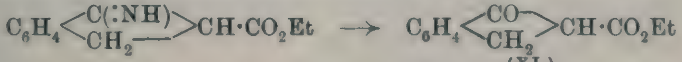
This oil proved to be the normal condensation product, namely, ethyl *o*-cyanobenzylmalonate, $CN\cdot C_6H_4\cdot CH_2\cdot CH(CO_2Et)_2$, and it was found that when an alcoholic solution of this substance containing a trace of sodium ethoxide was warmed, a carbethoxyl group was at once eliminated as ethyl carbonate, and the product described by Hausmann as ethyl *o*-cyano-β-phenylpropionate was formed. Subsequent investigation proved conclusively that this product is ethyl 1-iminohydrindene-2-carboxylate (IX), and that its formation in the manner described above is represented by the equation :



$$C_6H_4\left<\begin{matrix}CN\\ CH_2\cdot CH(CO_2Et)_2\end{matrix}\right. + EtOH \longrightarrow C_6H_4\left<\begin{matrix}C(:NH)\\ CH_2\end{matrix}\right>CH\cdot CO_2Et + CO(OEt)_2.$$

(IX.)

The proof of the constitution of this substance is as follows : When a solution of the imino-compound in alcohol is mixed with rather more than the quantity of concentrated hydrochloric acid necessary to hydrolyse the C:NH-group to carbonyl and the solution is warmed, ammonium chloride separates, and the solution on dilution yields an oil which boils at 185°/20 mm., and which gives in alcoholic solution an intense violet coloration with ferric chloride. This oil, which is without doubt ethyl 1-hydrindone-2-carboxylate (XI),

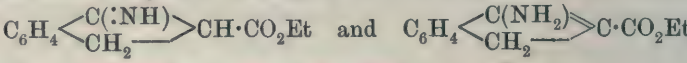


$$C_6H_4\left<\begin{matrix}C(:NH)\\ CH_2\end{matrix}\right>CH\cdot CO_2Et \longrightarrow C_6H_4\left<\begin{matrix}CO\\ CH_2\end{matrix}\right>CH\cdot CO_2Et$$

(XI.)

gives a well defined phenylhydrazone and semicarbazone, the same phenylhydrazone being also formed from the imino-compound (IX) when it is boiled in acetic acid solution with phenylhydrazine acetate.

The imino-compound is, as Gabriel and Hausmann showed, readily soluble in concentrated hydrochloric acid, and is precipitated on adding water. It is not, however, completely unchanged by this process, since a quantity, depending for amount on the length of time it is left in contact with the strong acid, is converted into the ketone. The process of conversion at the ordinary temperature is very slow, and the usual method adopted in other cases, of pouring the concentrated hydrochloric solution into hot water and cooling, converts only a small quantity of the imino-compound into the ketone. It is evident therefore that ethyl 1-iminohydrindene-2-carboxylate is a tautomeric amino-imino-compound reacting in the two forms:

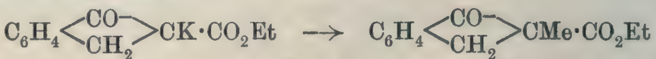


$$\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{C(:NH)}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{CH{\cdot}CO_2Et} \quad \text{and} \quad \mathrm{C_6H_4}{<}\begin{matrix}\mathrm{C(NH_2)}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{C{\cdot}CO_2Et},$$

but that it has only a short imino-phase.

Ethyl 1-hydrindone-2-carboxylate (XI) is readily soluble in dilute aqueous potassium hydroxide, but it is only slowly extracted from its solution in ether by means of aqueous sodium carbonate solution. Both the potassium and sodium salts are sparingly soluble in excess of the alkali, and can be readily isolated in a pure condition.

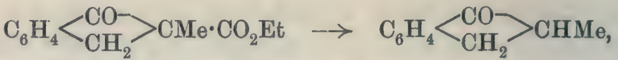
When the potassium salt (XII), either in the soluble or insoluble form, is boiled in alcohol with methyl iodide, the *C*-methyl derivative (XIII) is obtained as sole product, and no trace of the corresponding *O*-methyl ether could be detected:



$$\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CO}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{CK{\cdot}CO_2Et} \longrightarrow \mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CO}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{CMe{\cdot}CO_2Et}$$

(XII.) (XIII.)

The *C*-methyl derivative readily yields the corresponding 2-methyl-1-hydrindone when distilled in a current of steam from dilute sulphuric acid,



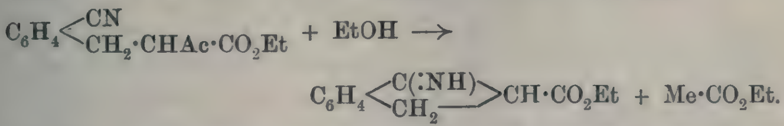
$$\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CO}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{CMe{\cdot}CO_2Et} \longrightarrow \mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CO}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{CHMe},$$

a process which is complete, owing to there being no tendency for the β-alkyl derivatives of α-hydrindone to undergo intramolecular condensation analogous to the formation of anhydro-bis-α-hydrindone (Trans., 1897, **71**, 241) from α-hydrindone. The direct formation of ethyl 1-iminohydrindene-2-carboxylate in the original condensation is, we find, best effected by working in the manner described above until the reaction is complete, and then, by adding excess of sodium ethoxide, to convert the open-chain compound into the hydrindene ring. The compound $\mathrm{CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}C(CO_2Et)_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CN}$, which is formed by the condensation of two molecules of *o*-cyanobenzyl chloride with one molecule of ethyl malonate, is so readily produced that if the condensation is effected in the usual way, the product consists for the most part of the more complex derivative.

(2) *The Condensation of Ethyl Sodioacetoacetate and* o-*Cyanobenzyl Chloride.*—It is hardly necessary in this condensation to take any precautions to prevent the formation of the derivative

$$\mathrm{CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}CAc(CO_2Et){\cdot}CH_2{\cdot}C_6H_4{\cdot}CN},$$

as under the ordinary conditions very little of it is formed. If, however, the method described in the experimental portion is used, the normal product (XII) can be readily isolated, and this compound on treatment with a trace of sodium ethoxide passes quantitatively into ethyl acetate and ethyl 1-iminohydrindene-2-carboxylate, thus :

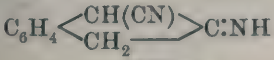


$$C_6H_4<\begin{matrix}CN\\CH_2\cdot CHAc\cdot CO_2Et\end{matrix} + EtOH \longrightarrow C_6H_4<\begin{matrix}C(:NH)\\CH_2\end{matrix}>CH\cdot CO_2Et + Me\cdot CO_2Et.$$

For the rapid preparation of this imino-compound in quantity this condensation produces the best results, the best method being to add an alcoholic solution of ethyl sodioacetoacetate containing a slight excess of sodium ethoxide to a hot alcoholic solution of the chloride.

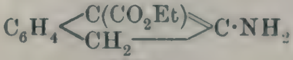
(3) *The Condensation of Ethyl Sodiocyanoacetate and* o-*Cyanobenzyl Chloride.*—The main object of investigating this condensation was to compare the derivatives of α-hydrindone with those of β-hydrindone in order to ascertain whether the phenomenon of "steric inhibition" which was so marked in the case of the β-compound substituted in the α-position applied also to the α-compound substituted in the β-position.

It has been found as regards the derivatives of β-hydrindone and its imino-derivative (Trans., 1908, **93**, 165), that the presence of certain groups on the α-carbon atom causes the compounds to react as true amino-derivatives, whereas certain other groups on this carbon atom cause the imino-form to be stable, and that this occurs irrespective of the acidity of the groups which we have hitherto shown to be the determining factor in deciding the amino- or imino-structure of a compound of this type. Thus the compound of formula (XIII*a*) evidently had the imino-structure, or rather exhibited amino-imino-tautomerism with a long imino-phase, whereas when the cyano-group was displaced by the less negative carbethoxyl group, the compound, instead of showing amino-imino-tautomerism with a longer imino-phase, as it should have done, behaved as a true amino-compound of formula (XIV) :



$$C_6H_4<\begin{matrix}CH(CN)\\CH_2\end{matrix}>C:NH$$

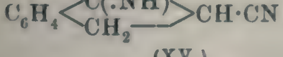
(XIII*a*.)



$$C_6H_4<\begin{matrix}C(CO_2Et)\\CH_2\end{matrix}>C\cdot NH_2$$

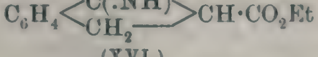
(XIV.)

It seemed of interest therefore to compare the corresponding derivatives of α-iminohydrindene of formulæ (XV) and (XVI)



$$C_6H_4<\begin{matrix}C(:NH)\\CH_2\end{matrix}>CH\cdot CN$$

(XV.)



$$C_6H_4<\begin{matrix}C(:NH)\\CH_2\end{matrix}>CH\cdot CO_2Et$$

(XVI.)

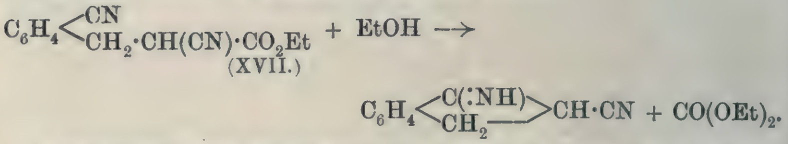
in order that a direct comparison might be made between the two series.

The condensation of *o*-cyanobenzyl chloride with the sodium compound of ethyl cyanoacetate, if carried out in the usual way, leads to the formation of the compound

$$\mathrm{CN\cdot C_6H_4\cdot CH_2\cdot C(CN)(CO_2Et)\cdot CH_2\cdot C_6H_4\cdot CN}$$

to the extent of 80 per cent. of the theoretical amount, and only a small quantity of ethyl 1-imino-2-cyanohydrindene (XV) is produced.

If, however, the precaution is taken of adding an alcoholic solution of the sodium salt of ethyl cyanoacetate to a hot alcoholic solution of *o*-cyanobenzyl chloride, a considerable yield of the normal condensation product (XVII) can be obtained, and this substance on treatment with sodium ethoxide passes at once into 1-imino-2-cyanohydrindene and ethyl carbonate in accordance with the scheme:



$$\mathrm{C_6H_4}<\begin{matrix}\mathrm{CN}\\ \mathrm{CH_2\cdot CH(CN)\cdot CO_2Et}\end{matrix} + \mathrm{EtOH} \longrightarrow \mathrm{C_6H_4}<\begin{matrix}\mathrm{C(:NH)}\\ \mathrm{CH_2}\end{matrix}>\mathrm{CH\cdot CN} + \mathrm{CO(OEt)_2}.$$

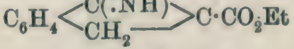
(XVII.)

A comparison of 2-imino-1-cyanohydrindene (XIII) with 1-imino-2-cyanohydrindene (XV) showed that these compounds did not possess any essential points of difference beyond what was to be expected from their structure. Thus the imino-group of 1-imino-2-cyanohydrindene is between the negative phenylene group and the nitrile group, whereas in the case of 2-imino-1-cyanohydrindene the negative influence of the phenylene group would be less pronounced. Consequently it might be anticipated that whilst both compounds would be tautomeric amino-imino-compounds, the 1-imino-derivative would possess a longer amino-phase than the 2-imino-derivative.

This anticipation is borne out by the experimental facts, for whereas 1-imino-2-cyanohydrindene, with its long amino-phase, dissolves readily in concentrated hydrochloric acid, forming a salt which, on the addition of water, is dissociated regenerating the amino-compound mixed with only a small quantity of the corresponding ketone, 2-imino-1-cyanohydrindene does not dissolve in concentrated hydrochloric acid, but when warmed with the acid is converted almost completely into the ketone. In other words, the rate of hydrolysis of the 2-imino-derivative is very much quicker than that of the 1-imino-derivative.

The two compounds therefore serve as admirable examples of the influence of negative groups on the predominance of the amino- or imino-phase in compounds exhibiting amino-imino-tautomerism.

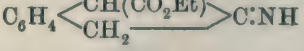
When the two carboxylic esters of formulæ (XVIII) and (XIX)



$$\mathrm{C_6H_4}<\begin{matrix}\mathrm{C(:NH)}\\ \mathrm{CH_2}\end{matrix}>\mathrm{C\cdot CO_2Et}$$

(XVIII.)

and



$$\mathrm{C_6H_4}<\begin{matrix}\mathrm{CH(CO_2Et)}\\ \mathrm{CH_2}\end{matrix}>\mathrm{C:NH}$$

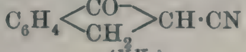
(XIX.)

are compared, a marked difference is at once apparent.

It has been already shown that ethyl 2-iminohydrindene-1-carboxylate (XIX) is a true amino-compound, which can be hydrolysed to the corresponding acid by means of hydrochloric acid without the nitrogen group being affected. Subsequent experiments showed that this behaviour was exhibited by other compounds having groups of large molecular volume attached to the 1-carbon atom, and hence it was suggested that the presence of a group of more than a certain volume did not permit of the attachment of the hydrogen atom to the 1-carbon atom. In other words, the compound ceased, under these conditions, to react in one of its tautomeric forms.

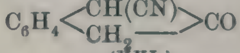
The examination of the behaviour of ethyl 1-iminohydrindene-2-carboxylate (XVIII) under similar conditions showed that, although the substitution of the carbethoxyl group for the nitrile group increased the amino-phase of the compound, that is to say, increased the length of time required for the hydrolysis of the compound to the ketone, yet it still exhibited well-defined amino-imino-tautomerism, and its hydrolysis to the ketone by acids was always completely effected. It is, of course, evident that as the carbethoxy-group possesses less negative properties than the nitrile group, the reverse should be the case, and it therefore follows that there must be a certain degree of steric hindrance attaching to the 1-carbon atom, but to a very much less extent than to the 2-carbon atom. An explanation of this fact is afforded by the consideration that the 1-carbon atom of ethyl 2-iminohydrindene-1-carboxylate is attached to both the phenylene group and the carbethoxyl group, whereas the 2-carbon atom of ethyl 1-iminohydrindene-2-carboxylate has only the carbethoxyl attached to it.

When the oxygen derivatives (XX) and (XXI) are compared, certain points of difference are also observed. Thus it has been shown that



$C_6H_4{<}\begin{matrix}CO\\CH_2\end{matrix}{>}CH{\cdot}CN$

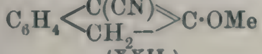
(XX.)



$C_6H_4{<}\begin{matrix}CH(CN)\\CH_2\end{matrix}{>}CO$

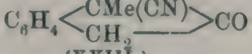
(XXI.)

1-cyano-2-hydrindone (XXI) yields a methoxy-derivative (XXII) when alkylated by the usual etherifying agents, but that when methylated



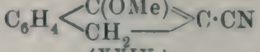
$C_6H_4{<}\begin{matrix}C(CN)\\CH_2\end{matrix}{>}C{\cdot}OMe$

(XXII.)



$C_6H_4{<}\begin{matrix}CMe(CN)\\CH_2\end{matrix}{>}CO$

(XXIII.)



$C_6H_4{<}\begin{matrix}C(OMe)\\CH_2\end{matrix}{>}C{\cdot}CN$

(XXIV.)

by means of sodium methoxide and methyl iodide it yields the *C*-methyl derivative (XXIII). With 2-cyano-1-hydrindone (XX) the increased negative character of the compound due to the proximity of the phenylene group is apparent, and the action of sodium methoxide and methyl iodide leads to the formation of the methoxy-derivative (XXIV) only.

As considerable quantities of the compounds containing two equivalents of *o*-cyanobenzyl chloride had accumulated during the preparation of the simpler products formed in these condensations, we investigated their properties. The cyano-derivative (XXV) formed in the ethyl cyanoacetate condensation is readily hydrolysed by dilute alkali, yielding an alkali salt, from which the acid (XXVI) is obtained by the action of mineral acids. When heated at 180°, this substance eliminates carbon dioxide and passes into the trinitrile (XXVII). When completely hydrolysed, the nitrile is converted into the tricarboxylic acid (XXVIII), a compound which is identical with that formed by the complete hydrolysis of the condensation products (XXIX) and (XXX) formed in the ethyl malonate and ethyl acetoacetate condensations respectively. The constitution of these more complex compounds is therefore clearly established.

$CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}C(CN)(CO_2Et){\cdot}CH_2{\cdot}C_6H_4{\cdot}CN$
(XXV.)

$CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}C(CN)(CO_2H){\cdot}CH_2{\cdot}C_6H_4{\cdot}CN$
(XXVI.)

$CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CN){\cdot}CH_2{\cdot}C_6H_4{\cdot}CN$
(XXVII.)

$CO_2H{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H$
(XXVIII.)

$CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}C(CO_2Et)_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CN$
(XXIX.)

$CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}CAc(CO_2Et){\cdot}CH_2{\cdot}C_6H_4{\cdot}CN$
(XXX.)

EXPERIMENTAL.

Ethyl o-*Cyanobenzylmalonate*, $CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CO_2Et)_2$.

This substance can be prepared in quantity by the condensation of ethyl sodiomalonate with *o*-cyanobenzyl chloride if care is taken not to have free sodium ethoxide present at any time during the course of the condensation. In order to effect this, it is necessary to add an alcoholic solution of the sodium compound of ethyl malonate to a hot alcoholic solution of the chloride, that is to say, in the reverse manner to that usually adopted in these condensations. The conditions found most favourable were as follows: 2·2 grams of sodium were dissolved in 50 c.c. of alcohol and mixed with 16 grams of ethyl malonate, the warm solution being then slowly added to a hot solution of 15 grams of *o*-cyanobenzyl chloride dissolved in the requisite amount of alcohol. The reaction was allowed to proceed by its own heat, and was completed by heating on the water-bath for five minutes, when the solution was found to be neutral. Water was then added, and the alcohol and unchanged ethyl malonate separated by distillation in a current of steam, the heavy, non-volatile oil being subsequently extracted by ether. The residue which remained after evaporating the ether yielded a large fraction, boiling at 213°/20 mm., consisting of a viscid, colourless oil:

0·1958 gave 0·4722 CO_2 and 0·1080 H_2O. C = 65·77; H = 6·13.
$C_{15}H_{17}O_4N$ requires C = 65·4; H = 6·2 per cent.

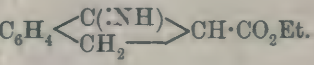
The ethyl salt is unchanged by cold concentrated hydrochloric acid, and its open-chain structure is proved by the fact that when boiled for a long time with dilute sulphuric acid, it is slowly hydrolysed, and the solution on cooling deposits a crystalline acid, which, when recrystallised from water, yields long needles, melting at 166°. (Found, C = 61·72; H = 5·3. Calc., C = 61·8; H = 5·2 per cent.)

The acid is therefore *o*-carboxy-β-phenylpropionic acid,

$$CO_2H\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO_2H.$$

During the fractionation of ethyl *o*-cyanobenzylmalonate a small quantity of lower boiling material was obtained, which solidified after some time, and, on examination, proved to be ethyl 1-iminohydrindene-2-carboxylate (see p. 2273). There was also a small amount of higher fraction boiling at about 300°/20 mm., which also solidified, and proved on investigation to be ethyl di-*o*-cyanobenzylmalonate (see p. 2280).

Ethyl 1-*Iminohydrindene-2-carboxylate*,



$$C_6H_4<\substack{C(:NH)\\CH_2}>CH\cdot CO_2Et.$$

This substance may be prepared in one of two ways, namely:

(1) *By the Action of Alcoholic Sodium Ethoxide on Ethyl* o-*Cyanobenzylmalonate.*—This method, which gives a quantitative yield of the imino-compound, can be carried out as follows: 10 grams of the ethyl salt are diluted with twice its volume of alcohol, and 1 c.c. of a solution of 1 gram of sodium in 12 c.c. of alcohol is added. The solution, which becomes appreciably warm, is kept for fifteen minutes, when it is warmed on the water-bath for five minutes and then poured into an equal volume of water. The crystals which separate are then collected and recrystallised from dilute alcohol.

The mother liquor from the crystals was extracted with ether, and the residue, after evaporating the ether, carefully fractionated under the ordinary pressure. A fraction boiling at 126—127° was ultimately obtained, which analysis showed to be ethyl carbonate. (Found, C = 50·65; H = 8·6. Calc., C = 50·8; H = 8·5 per cent.)

(2) *By the Direct Condensation of Ethyl Sodiomalonate and* o-*Cyanobenzyl Chloride.*—This method was that used by Gabriel and Hausmann, but under the conditions employed by them, we find that the greater portion of the product consists of ethyl di-*o*-cyanobenzylmalonate, and only a small yield of the imino-compound can be obtained. It is men-

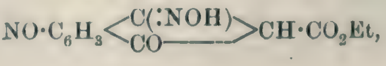
tioned later (p. 2279) that the best method for preparing this imino-compound in quantity is by employing the sodium compound of ethyl acetoacetate instead of ethyl sodiomalonate in the condensation, because in that case very little of the di-derivative is formed. A good yield of the imino-compound can, however, be obtained from ethyl malonate if the conditions described in the preparation of ethyl *o*-cyanobenzylmalonate (p. 2270) are closely followed, and, as soon as the condensation mixture has become neutral, a small quantity of alcoholic sodium ethoxide is added, and the heating continued for five minutes longer. When the product obtained in this way is poured into water, it will be found that the whole of the dicarboxylic ester has been converted into the imino-compound and ethyl carbonate, and that it will deposit a large quantity of oil which will solidify on scratching. This solid, which consists of the imino-compound mixed with some ethyl di-*o*-cyanobenzylmalonate, can be separated by the method used by Gabriel and Hausmann, that is, by dissolving the imino-compound in concentrated hydrochloric acid and filtering the solution from the undissolved di-derivative. On diluting the filtrate, a certain amount of the imino-compound separates in the crystalline form, but the separation is by no means complete, as the substance is appreciably soluble in dilute hydrochloric acid. In order to obtain the whole amount, it is necessary to extract the diluted acid solution with ether.

Ethyl 1-*iminohydrindene*-2-*carboxylate* crystallises from dilute alcohol in colourless needles, which melt at 98°. It gives no coloration with ferric chloride:

0·1923 gave 0·4970 CO_2 and 0·1060 H_2O. C = 70·49; H = 6·10.
$C_{12}H_{13}O_2N$ requires C = 70·9; H = 6·4 per cent.

The mother liquor from the recrystallisation of the imino-compound gives an intense blue coloration with ferric chloride, showing that the treatment with hydrochloric acid had converted some of it into the corresponding ketone. When treated in hot acetic acid solution with phenylhydrazine acetate it yields the same hydrazone, melting at 101·5°, as that derived from the ketone (p. 2273). It is insoluble in aqueous potassium hydroxide, and is only slowly hydrolysed on boiling with this reagent.

Action of Nitrous Acid.—When the imino-compound is dissolved in concentrated hydrochloric acid and mixed when very cold with excess of sodium nitrite solution, an oil is precipitated which solidifies after some time. When this substance is recrystallised from alcohol, it is obtained in brilliant yellow leaflets, which melt at 163° with vigorous decomposition and charring. Analysis points to the formula



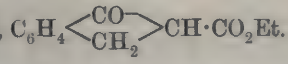
$$NO\cdot C_6H_3<\begin{matrix}C(:NOH)\\CO\end{matrix}>CH\cdot CO_2Et,$$

but the position of the nitroso-group in the ring is uncertain:

0·1765 gave 0·3559 CO_2 and 0·0632 H_2O. C = 54·99; H = 3·95.

$C_{12}H_{10}O_5N_2$ requires C = 55·0; H = 3·8 per cent.

Ethyl 1-*Hydrindone*-2-*carboxylate*,



$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CH_2}>CH\cdot CO_2Et.$$

Ethyl 1-iminohydrindone-2-carboxylate is only very slightly changed when its solution in concentrated hydrochloric acid is poured into boiling water, conditions which completely hydrolyse the corresponding nitrile to the ketone (see p. 2277). The hydrolysis can, however, be completely effected in the following manner: Ten grams of the imino-compound are dissolved in 50 c.c. of alcohol, and rather more than the calculated quantity of concentrated hydrochloric acid is added. The solution is then boiled for three minutes, during which time a large quantity of ammonium chloride separates. It is then cooled and mixed with a large volume of water, when a heavy oil is deposited, which is extracted by ether. The ethereal solution, when freed from impurities by washing first with water and then with sodium carbonate solution, leaves, on evaporation, an oil which distils at 185°/20 mm. as a viscid, colourless liquid. The distillation can only be accomplished with small quantities, otherwise rapid decomposition ensues:

0·2169 gave 0·5593 CO_2 and 0·1168 H_2O. C = 70·33; H = 5·98.

$C_{12}H_{12}O_3$ requires C = 70·6; H = 5·9 per cent.

Ethyl 1-*hydrindone*-2-*carboxylate* gives in alcoholic solution an intense blue coloration with ferric chloride. It is soluble in dilute aqueous potassium hydroxide and in cold alkaline carbonate solutions, but it cannot be extracted from its solution in ether by shaking with these reagents. When excess of aqueous potassium hydroxide is added to a solution of the ketone in the dilute alkali, a sparingly soluble *potassium* salt separates. When freshly precipitated, this salt is readily soluble in both ethyl and methyl alcohol, but if the solution in either of these solvents is kept, colourless, silky needles separate, which are very sparingly soluble in hot alcohol:

0·3192 gave 0·1127 K_2SO_4. K = 15·83.

$C_{12}H_{11}O_3K$ requires K = 16·1 per cent.

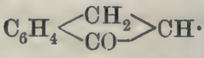
It is probable that the salt when first precipitated contains water of crystallisation, although no satisfactory analysis could be made of the hydrated product.

The *phenylhydrazone*, $C_{18}H_{18}O_2N_2$, is formed when either the ketone or the imino-compound, dissolved in glacial acetic acid, is mixed with a solution of phenylhydrazine acetate and boiled. It separates as an oil on dilution, and solidifies on scratching. When recrystallised from alcohol, it forms pale yellow needles, which melt at 101·5°:

0·1861 gave 0·5001 CO_2 and 0·1036 H_2O. C = 73·30 ; H = 6·13.
$C_{18}H_{18}O_2N_2$ requires C = 73·5 ; H = 6·1 per cent.

The *semicarbazone*, $C_{13}H_{15}O_3N_3$, is precipitated when a solution of the ketone in dilute alcohol is mixed with an aqueous solution of semicarbazide acetate. It crystallises from dilute acetic acid in slender needles, which melt and char at 200°:

0·1445 gave 0·3161 CO_2 and 0·0756 H_2O. C = 59·66 ; H = 5·81.
$C_{13}H_{15}O_3N_3$ requires C = 59·8 ; H = 5·8 per cent.

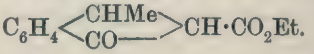
1-*Hydrindone-2-carbanilide*,  $C_6H_4<{CH_2 \atop CO}>CH{\cdot}CO{\cdot}NHPh$, is formed when the ethyl salt is boiled with an equal volume of aniline for five minutes and the solution is poured into dilute hydrochloric acid. It crystallises from alcohol in colourless, lustrous plates, which melt at 177°:

0·1560 gave 0·4369 CO_2 and 0·0754 H_2O. C = 76·38 ; H = 5·37.
$C_{16}H_{13}O_2N$ requires C = 76·5 ; H = 5·2 per cent.

a-Hydrindone.

This ketone is most conveniently prepared by passing a current of steam through ethyl 1-hydrindone-2-carboxylate or the imino-compound suspended in boiling 10 per cent. sulphuric acid. The ketone passes over with the steam, and solidifies in the receiver. It melted at 41°, and was characterised by conversion into the semicarbazone melting at 237°. The formation of anhydro-bishydrindene was not observed, the yield of the ketone being practically quantitative.

Ethyl 3-*Methyl*-1-*hydrindone*-2-*carboxylate*,



$$C_6H_4<{CHMe \atop CO}>CH{\cdot}CO_2Et.$$

This compound may be prepared in the following way: Eight grams of ethyl 1-hydrindone-2-carboxylate are added to a solution containing 1 gram of sodium dissolved in 20 c.c. of alcohol, when a copious precipitation of the sodium salt takes place. Excess of methyl iodide is then added, and the mixture is heated on the water-bath until the sodium compound, which is practically insoluble in hot alcohol, has all passed into solution. The product is then freed from alcohol by evaporation on the water-bath, diluted with water, and the oil which is then precipitated is extracted by ether. The ethereal extract, after being washed with sodium carbonate solution, is dried and evaporated, when it leaves an oil which distils at 181°/20 mm. as a moderately viscid, colourless liquid:

0·1848 gave 0·4817 CO_2 and 0·1848 H_2O. C = 71·09 ; H = 6·70.
$C_{13}H_{14}O_3$ requires C = 71·6 ; H = 6·4 per cent.

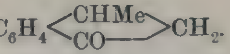
Ethyl 3-methyl-1-hydrindone-2-carboxylate is insoluble in aqueous potassium hydroxide, and gives no coloration in alcoholic solution with ferric chloride.

The *semicarbazone*, $C_{14}H_{17}O_3N_3$, is precipitated when a solution of the ketone in dilute alcohol is mixed with an aqueous solution of semicarbazide acetate. It separates from dilute methyl alcohol in clusters of small needles, which melt at 150°:

0·1692 gave 0·3794 CO_2 and 0·0956 H_2O. C = 61·14; H = 6·28.

$C_{14}H_{17}O_3N_3$ requires C = 61·1; H = 6·2 per cent.

3-*Methyl*-1-*hydrindone*,



$$C_6H_4<\substack{CHMe\\CO}>CH_2.$$

This substance is formed when ethyl 3-methyl-1-hydrindone-2-carboxylate, suspended in 20 per cent. sulphuric acid, is treated with a current of steam. The ketone, as it is formed, passes over with the steam, and can be obtained as a colourless liquid, boiling at 250°/756 mm., on extracting the distillate with ether:

0·1693 gave 0·5118 CO_2 and 0·1080 H_2O. C = 82·46; H = 7·01.

$C_{10}H_{10}O$ requires C = 82·2; H = 6·8 per cent.

The *phenylhydrazone*, $C_{16}H_{16}N_2$, separates as an oil, which solidifies on scratching, when a hot solution of the ketone in dilute acetic acid is mixed with a hot solution of phenylhydrazine acetate. It crystallises from dilute alcohol in glistening yellow plates, melting at 95°:

0·1684 gave 0·5025 CO_2 and 0·1035 H_2O. C = 81·27; H = 6·69.

$C_{16}H_{16}N_2$ requires C = 81·4; H = 6·8 per cent.

The *semicarbazone*, $C_{11}H_{13}ON_3$, prepared in the usual way, crystallises from dilute alcohol in slender needles, melting at 190°:

0·1049 gave 0·2493 CO_2 and 0·0614 H_2O. C = 64·81; H = 6·50.

$C_{11}H_{13}ON_3$ requires C = 65·0; H = 6·4 per cent.

Ethyl α-o-Dicyano-β-phenylpropionate, $CN\cdot C_6H_4\cdot CH_2\cdot CH(CN)\cdot CO_2Et$.

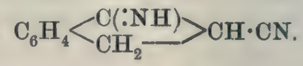
—The condensation of *o*-cyanobenzyl chloride with the sodium compound of ethyl cyanoacetate, if carried out in the usual manner, yields very little of the above product or of ethyl 1-imino-2-cyanohydrindene, the chief compound formed being ethyl α-*oo*-tricyano-ββ′-diphenyl*iso*butyrate, which is produced to the extent of about 80 per cent. of the theoretical quantity. If, however, the condensation is effected in the following manner, a good yield of the normal product can be obtained: Two grams of sodium are dissolved in 50 c.c. of alcohol, and 10·3 grams of ethyl cyanoacetate are added, the solution being kept warm in order to prevent the sodium compound from caking. The hot sodium compound is then added to a hot solution of 13·5 grams of *o*-cyanobenzyl chloride in 20 c.c. of alcohol, and the mixture kept hot until the reaction is finished. The bulk of the alcohol is then distilled off, and the residue diluted with water, when an oil separates which becomes partly solid. On extracting with ether, the solid, which was found to be ethyl *a*-*oo*-tricyano-*ββ'*-diphenyl*iso*butyrate (see p. 2280), remains undissolved, and can be separated from the ethereal solution of the oil by filtration. The residue left on evaporating the dried ethereal extract is then distilled under diminished pressure. It is a viscid, colourless liquid, which boils at 220°/20 mm.:

0·1921 gave 0·4844 CO_2 and 0·0934 H_2O. C = 68·77; H = 5·40.

$C_{13}H_{12}O_2N_2$ requires C = 68·9; H = 5·3 per cent.

Ethyl a-o-*dicyano-β-phenylpropionate* does not dissolve in cold concentrated hydrochloric acid. Its structure is shown by the formation of *o*-carboxy-*β*-phenylpropionic acid from it on complete hydrolysis with dilute sulphuric acid.

1-*Imino-2-cyanohydrindene*,



$$C_6H_4{<}\begin{matrix}C(:NH)\\CH_2\text{——}\end{matrix}{>}CH\cdot CN.$$

This substance may be prepared either by the action of sodium ethoxide on ethyl *a*-*o*-dicyano-*p*-phenylpropionate, or by the direct condensation of *o*-cyanobenzyl chloride with the sodium compound of ethyl cyanoacetate in the presence of excess of sodium ethoxide.

(1) *From Ethyl a*-o-*Dicyano-β-phenylpropionate.*—In this preparation 10 grams of the dicarboxylic ester are dissolved in 25 c.c. of alcohol, and mixed with 1 c.c. of a solution of sodium ethoxide containing 1 gram of sodium dissolved in 10 c.c. of alcohol. The solution, which becomes brown in colour, is then warmed on the water-bath for five minutes, when it is cooled and diluted with an equal volume of water. Crystals separate on scratching, which, when recrystallised from benzene, form large prisms, melting at 137°.

The mother liquor from the condensation, when extracted by ether, yields a residue on evaporating the solvent, which when carefully fractionated furnishes a considerable amount of ethyl carbonate, boiling at 126°. (Found, C = 50·58; H = 8·61. Calc., C = 50·8; H = 8·5 per cent.)

(2) *From Ethyl Sodiocyanoacetate and* o-*Cyanobenzyl Chloride.*—This method of preparation always yields the imino-nitrile mixed with some ethyl *a*-*oo*-tricyano-*ββ'*-diphenyl*iso*butyrate, from which it cannot be readily separated. If the ketone is required, it can be quickly isolated pure by this means, because it is only necessary to treat the mixture with hot dilute hydrochloric acid, extract with ether, and shake out the ketone by means of sodium carbonate solution, in order

to obtain the pure product on acidifying the alkaline extract. Owing to the ease with which the imino-compound is hydrolysed to the ketone by hydrochloric acid, it is not advisable to separate the mixture by the aid of this reagent. Ultimately the following process was found to give satisfactory results.

The condensation was effected in the same manner as described for ethyl *a-o*-dicyano-*p*-phenylpropionate (see p. 2275), and when the reaction was finished a slight excess of sodium ethoxide was added and the heating continued for fifteen minutes. Water was then added, and the solid which separated was collected. It was then rubbed with cold methyl alcohol, filtered from the undissolved di-derivative, and precipitated from the methyl-alcoholic solution by the addition of water.

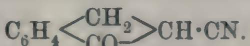
After this process had been repeated twice, the dried product was recrystallised from benzene, when it was obtained in large prisms, melting at 137°:

0·1898 gave 0·5346 CO_2 and 0·0907 H_2O. C = 76·83; H = 5·31.

$C_{10}H_8N_2$ requires C = 76·9; H = 5·1 per cent.

1-*Imino*-2-*cyanohydrindene* is at once soluble in cold concentrated hydrochloric acid. When treated in hot acetic acid solution with a solution of phenylhydrazine acetate, it yields the same hydrazone as 2-cyano-1-hydrindone (see p. 2278).

2-*Cyano*-1-*hydrindone*,



$C_6H_4<\begin{matrix}CH_2\\CO\end{matrix}>CH\cdot CN.$

This compound is readily prepared from 1-imino-2-cyanohydrindene by hydrolysis with dilute hydrochloric acid, for which purpose the following conditions were found to give the best results. Ten grams of the imino-compound were dissolved in concentrated hydrochloric acid, and the clear solution poured into twice its volume of boiling water, the solution being cooled as quickly as possible after the addition of the acid. An oil separated, which was extracted by ether, the ethereal extract being shaken with dilute sodium carbonate solution. The alkaline extract was then acidified, when an oil was precipitated which solidified on scratching. When collected and recrystallised from dilute alcohol, it formed small, colourless needles, melting at 73°:

0·1738 gave 0·4845 CO_2 and 0·0712 H_2O. C = 76·03; H = 4·55.

$C_{10}H_7ON$ requires C = 76·4; H = 4·5 per cent.

2-*Cyano*-1-*hydrindone* is readily soluble in dilute alkaline carbonate solutions. When dissolved in dilute aqueous potassium hydroxide, the *potassium* salt separates on the addition of excess of the alkali. The ketone gives a green coloration in alcoholic solution with ferric chloride.

The *phenylhydrazone*, $C_{16}H_{13}N_3$, is precipitated when a solution of the ketone in dilute acetic acid is warmed with a solution of phenylhydrazine acetate. It separates from alcohol in pale yellow needles, melting at 160°:

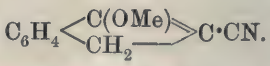
0·1797 gave 0·5110 CO_2 and 0·0851 H_2O. C = 77·55; H = 5·26.
$C_{16}H_{13}N_3$ requires C = 77·7; H = 5·3 per cent.

The O-*benzoyl* derivative, $C_{17}H_{11}O_2N$, can be prepared in small yield by the Schotten-Baumann method. It crystallises from alcohol in long, colourless needles, melting at 101·5°:

0·1355 gave 0·3884 CO_2 and 0·500 H_2O. C = 78·16; H = 4·10.
$C_{17}H_{11}O_2N$ requires C = 78·1; H = 4·2 per cent.

When 2-cyano-1-hydrindone is boiled with dilute sulphuric acid (10 per cent.) for five hours and the product is distilled in a current of steam, α-hydrindone is formed, and passes over with the steam.

2-*Cyano-3-methoxyindene*,



$C_6H_4\Big<\begin{matrix}C(OMe)\\CH_2\end{matrix}\Big>C\cdot CN.$

The above methoxy-derivative is the sole product of the methylation of 2-cyano-1-hydrindone whether the alkylation is carried out by means of sodium methoxide and methyl iodide or whether the pure potassium salt is used for the purpose. The preparation can be conveniently effected as follows: The potassium salt prepared by the addition of excess of potassium hydroxide to a solution of the ketone in dilute alkali is purified by rubbing with cold ethyl alcohol, and is then suspended in methyl alcohol and treated with excess of methyl iodide. The mixture is heated on the water-bath until all the salt has passed into solution, when it is evaporated on the water-bath and treated with water. The oil which is then precipitated is extracted with ether, and the ethereal extract dried and evaporated. The residue distils at 185°/20 mm. as a clear, colourless oil, which is quite insoluble in cold alkali:

0·2013 gave 0·5691 CO_2 and 0·0978 H_2O. C = 77·11; H = 5·4.
$C_{11}H_9ON$ requires C = 77·2; H = 5·3 per cent.

The methoxy-structure of the compound is clearly shown by its behaviour on hydrolysis, for when it is treated with warm aqueous potassium hydroxide it slowly dissolves, and when the solution is acidified a crystalline substance melting at 73° is deposited. This compound was shown by direct comparison to be identical with 2-cyano-1-hydrindone.

Ethyl o-*Cyano-α-benzylacetoacetate*, $CN\cdot C_6H_4\cdot CH_2\cdot CHAc\cdot CO_2Et$.

The conditions employed in preparing this substance were as follows: 21·7 Grams of ethyl acetoacetate were added to an alcoholic solution containing 3·5 grams of sodium, and the mixture slowly added while hot to a hot solution of 25 grams of *o*-cyanobenzyl chloride in 25 c.c. of alcohol. The reaction was vigorous, and when all the sodium compound had been added, the product was found to give a neutral reaction. The greater portion of the alcohol was then distilled off and the residue mixed with water, when an oil separated, which was extracted by ether. The product obtained, after evaporating the dried ethereal solution, boiled at 210°/20 mm., forming a viscid, colourless liquid:

0·1972 gave 0·4947 CO_2 and 0·1100 H_2O. C = 68·47; H = 6·19.

$C_{14}H_{15}O_3N$ requires C = 68·6; H = 6·1 per cent.

Ethyl o-*cyano-a-benzylacetoacetate* is not affected by cold concentrated hydrochloric acid, and on complete hydrolysis with dilute sulphuric acid yields *o*-carboxy-*β*-phenylpropionic acid.

The Transformation of Ethyl o-*Cyano-a-benzylacetoacetate into Ethyl* 1-*Iminohydrindene*-2-*carboxylate.*

This conversion was effected by the action of sodium ethoxide in the following manner: Ten grams of the ester were dissolved in alcohol, treated with 1 c.c. of a 10 per cent. solution of sodium ethoxide in alcohol, and then warmed on the water-bath for fifteen minutes. At the end of this time the solution, which had a strong odour of ethyl acetate, was mixed with water, and the solid which then separated was filtered. When recrystallised from dilute alcohol it was melted at 98°, and was proved, by direct comparison, to be identical with ethyl 1-iminohydrindene-2-carboxylate.

The aqueous mother liquor from the condensation was saturated with ammonium sulphate and extracted with ether, the ethereal extract being washed with calcium chloride solution to remove alcohol, dried, and fractionated. The fraction boiling at 78° was collected, and proved from its odour and analysis to be ethyl acetate. (Found, C = 54·49; H = 9·21. Calc., C = 54·7; H = 9·1 per cent.)

When ethyl 1-iminohydrindene-2-carboxylate is required in large quantities, the best method for its preparation is the direct condensation of ethyl sodioacetoacetate and *o*-cyanobenzyl chloride in the presence of a slight excess of sodium ethoxide, because in this condensation the formation of the di-derivative does not take place to any appreciable extent. The product of the condensation, which solidifies on pouring into water, is separated in a pure condition by dissolving in concentrated hydrochloric acid, filtering, and extracting the filtrate after dilution with water with ether. The yield of ethyl 1-iminohydrindene-2-carboxylate under these conditions is 80 per cent. of the theoretical.

*The Di-*o*-cyanobenzyl Derivatives Formed in the Foregoing Condensations.*

Ethyl di-*o*-cyanobenzylmalonate, $(CN\cdot C_6H_4\cdot CH_2)_2C(CO_2Et)_2$, and ethyl di-*o*-cyanobenzylacetoacetate, $(CN\cdot C_6H_4\cdot CH_2)_2CAc\cdot CO_2Et$, obtained as by-products in the condensations of *o*-cyanobenzyl chloride with ethyl sodiomalonate and ethyl sodioacetoacetate respectively, have been prepared and described by Gabriel and Hausmann (*loc. cit.*), but they were not further investigated. The following is a description of the products which these compounds yield on hydrolysis, as well as of those derived from ethyl *a-oo*-tricyano-*ββ'*-diphenyl*iso*butyrate, which has not been prepared before.

*Ethyl a-oo-Tricyano-ββ'-diphenyl*iso*butyrate,* $(CN\cdot C_6H_4\cdot CH_2)_2C(CN)\cdot CO_2Et$.

This substance is obtained as a by-product in the condensation of ethyl sodiocyanoacetate with *o*-cyanobenzyl chloride, and remains undissolved after the imino-nitrile has been separated by the method described on page 2276. It separates from alcohol in small, colourless needles, melting at 123°:

0·2121 gave 0·5695 CO_2 and 0·1002 H_2O. C = 73·27; H = 5·25.

$C_{21}H_{17}O_2N_3$ requires C = 73·5; H = 5·0 per cent.

The ester is sparingly soluble in ether.

*a-oo-Tricyano-ββ'-diphenyl*iso*butyric Acid,* $(CN\cdot C_6H_4\cdot CH_2)_2C(CN)\cdot CO_2H$.

When ethyl *a-oo*-tricyano-*ββ'*-diphenyl*iso*butyrate is warmed with aqueous potassium hydroxide, it passes into solution, and if, when all has dissolved, the solution is cooled, an oily *potassium* salt separates, which dissolves on the addition of more water. On acidification, the clear solution deposits an oil which solidifies on stirring, and the solid can then be recrystallised from hot alcohol, from which solvent it separates as a microcrystalline powder melting at 175° with vigorous evolution of gas:

0·1508 gave 0·3988 CO_2 and 0·0569 H_2O. C = 72·12; H = 4·18.

$C_{19}H_{13}O_2N_3$ requires C = 72·4; H = 4·1 per cent.

oo-*Dicyano-ββ'-diphenyl*iso*butyronitrile*, $(CN\cdot C_6H_4\cdot CH_2)_2CH\cdot CN$.

This substance is formed when the above carboxylic acid is heated at 170° in a bath of sulphuric acid until all carbon dioxide has been evolved. The dark-coloured residue solidifies on being rubbed with ether, and at the same time becomes colourless. It may be further purified by recrystallisation from methyl alcohol, from which solvent it separates in large, flattened needles, melting at 132—133°:

0·1733 gave 23·2 c.c. N_2 at 18° and 733 mm. N = 15·3.

$C_{18}H_{13}N_3$ requires N = 15·5 per cent.

The trinitrile is readily soluble in hot methyl or ethyl alcohol and in hot benzene. It is sparingly soluble in ether or light petroleum.

oo-*Dicarboxy-ββ′-diphenyl*iso*butyric Acid*, $(CO_2H\cdot C_6H_4\cdot CH_2)_2CH\cdot CO_2H$.

This acid is formed by the ultimate hydrolysis of the di-*o*-cyanobenzyl derivatives described above.

From Ethyl α-oo-*Tricyano-ββ′-diphenyl*iso*butyrate.*—The ester is dissolved in concentrated sulphuric acid, and water is added until the solution just remains clear, when it is boiled on the sand-bath until an oil begins to separate. More water is then added until the solution is clear, when it is again heated until oil begins to separate. This process is continued for two hours, when the solution, which on cooling deposits large quantities of oil, is extracted by ether. When the ethereal extract is shaken with aqueous sodium carbonate and the alkaline extract acidified, a gummy acid is precipitated, which readily solidifies when rubbed with methyl alcohol, and crystallises from dilute alcohol in small needles, melting at 210°.

*From Ethyl Di-*o*-cyanobenzylmalonate.*—When this ester is boiled with an alcoholic solution containing one and a-half times the quantity of potassium hydroxide calculated for complete hydrolysis, and the heating is continued until all ammonia has apparently been given off, the solution on evaporating and acidifying yields a resinous acid. When this resin is extracted by ether, a large quantity of crystalline solid remains undissolved by the ether, and can be isolated by filtration. It can be recrystallised from much hot water, and is then obtained in small needles, melting at 227°. The analysis and properties of this substance showed it to be the *acid diamide* of the formula

$$(NH_2\cdot CO\cdot C_6H_4\cdot CH_2)_2CH\cdot CO_2H:$$

0·1820 gave 0·4430 CO_2 and 0·0942 H_2O. C = 66·38 ; H = 5·76.

$C_{18}H_{18}O_4N_2$ requires C = 66·3 ; H = 5·5 per cent.

The following titration was also made: 0·2600 required 8·1 c.c. of *N*/10-NaOH for neutralisation, whereas this amount of a monobasic acid, $C_{18}H_{18}O_4N_2$, requires 8·00 c.c.

The acid diamide when boiled for some time with excess of aqueous potassium hydroxide evolves ammonia, and the solution on acidifying yields a gummy acid, which soldifies on rubbing with alcohol. When recrystallised from dilute alcohol it forms small needles, melting at

210°, which are identical with those of the acid prepared from ethyl *a-oo*-tricyano-$\beta\beta'$-diphenyl*iso*butyrate:

0·1735 gave 0·4190 CO_2 and 0·0777 H_2O. C = 65·86; H = 4·97.

$C_{18}H_{16}O_6$ requires C = 65·9; H = 4·9 per cent.

The ethereal solution after the separation of the above acid diamide yields an oily residue on evaporation, which solidifies when rubbed with alcohol. It crystallises from dilute alcohol in yellow prisms, which melt at 142°, and yields a semicarbazone melting at 256°. We have not as yet succeeded in assigning any satisfactory formulæ to these substances.

Some of the expense entailed by this research has been met by grants from the Government Grant Committee of the Royal Society, for which we desire to express our indebtedness.

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CCXXXIX.—*Lead Silicates in Relation to Pottery Manufacture. Part II.*

By SIR EDWARD THORPE AND CHARLES SIMMONDS.

SOME years ago, in connexion with the question of lead poisoning in the pottery industry, we made a study of various complex lead silicates employed in the production of ceramic glazes ("Lead Silicates in Relation to Pottery Manufacture," Trans., 1901, **79**, 792). In particular, we showed that the quantity of lead which could be dissolved from a silicate by dilute acids depended primarily on the type of silicate. Monosilicates are easily attackable. Polysilicates and disilicates are but slightly so, and this is the case whether they contain little or much lead. We further showed that in the case of the polysilicates and disilicates, as ordinarily prepared, there is frequently a small quantity of an easily soluble lead compound mixed with the bulk; this could be extracted with dilute acid, leaving the residue practically unattackable under the conditions of the experiment.

A fairly complete summary of present knowledge of lead silicates and glazes in respect of the foregoing properties has recently been published by Beck, Löwe, and Stegmüller,* who have studied the action of acids both on the powdered silicate and on the fused glaze as it exists on the finished pottery ware. With certain modifications, they have repeated our experiments; but whereas our studies, made on silicates in actual commercial use, were of necessity chiefly concerned with the complex silicates, containing not only lead but other bases, Beck, Löwe, and Stegmüller have adopted what in some respects is the better plan of studying first the simple lead silicates.

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* "Zur Kenntniss der bleihaltigen Glasuren und deren Bleiabgabe an saure Flüssigkeiten" (*Arbeit. K. Gesundheitsamte*, 1910, **33**, No. 2).

The results they obtain lead, however, to the same conclusions as our own. Thus the proportion of lead oxide dissolved from three simple silicates was found to be as follows:

Silicate	PbO present grams	PbO dissolved by 1 per cent. HNO_3.	
		Amount	Percentage of total PbO
PbO,SiO_2	1·529	1·525	99·7
$PbO,2SiO_2$............	1·232	0·106	8·6
$PbO,3SiO_2$............	1·038	0·019	1·9

That is, practically all the lead is dissolved from the monosilicate, but a relatively small quantity only from the disilicate and trisilicate.

On a further treatment of the di- and tri-silicate residues, very little additional lead was extracted (0·5 and 0·6 per cent. respectively). This confirms what has already been stated (*loc. cit.*, p. 802).

An explanation of the fact that a single treatment with acid extracts substantially the whole of the "soluble" lead from the di- and the trisilicates is suggested by the German authors. At the temperature of fusion a certain amount of dissociation may occur; thus the disilicate $PbSi_2O_5$ may partly dissociate into $PbO + 2SiO_2$, or into $PbSiO_3 + SiO_2$, and a portion of these components may remain dissociated when the silicate cools. Since both lead oxide and monosilicate are readily soluble in dilute acids, they would, if the silicate were sufficiently finely powdered, be all extracted on a single treatment with acid, whilst even from a relatively coarse powder the bulk of this "soluble" lead would be removed.

In the paper quoted we give a table (pp. 796—797) illustrating the fact that whether a lead silicate yields much soluble lead or not depends mainly on the value of the ratio: number of acidic molecules/number of basic molecules. Beck, Löwe, and Stegmüller remark that whilst this appears capable of rendering good service for rapid sorting-out purposes, it gives no special insight into the effect of a particular constituent in individual cases. They note that the effects of boric oxide and alumina are contrary to what would be expected from the table, and suggest that the possibility of the formation of complex borosilicates and aluminosilicates may have been overlooked. Also they remark that the possibility of alumina acting as an acidic oxide must not be excluded (*loc. cit.*, p. 226).

The authors in question, however, have quoted the table from a

Parliamentary Paper in which it was reproduced ("Lead Compounds in Pottery," 1901, Cd. 679, p. 26—27). On reference to the original paper already referred to (*loc. cit.*, p. 799), it will be seen that the points they mention had not been lost sight of. We note there that "subsidiary factors may exist in the possible different states of combination in which alumina and boric oxide may occur in the silicate"; and we also say "it is conceivable that in some cases the alumina may act as an acid constituent. In such cases, the amount of lead dissolved would presumably be less than indicated by the value of the ratio." Further on we briefly discussed the influence of boric oxide.

These views, put forward tentatively, were arrived at from a comparison of the results yielded by various complex silicates of very diverse composition; but it was recognised that the best way of studying the matter was to ascertain the effect of each oxide singly rather than to deduce it from such comparisons.

A number of silicates were therefore prepared by fusion of the ingredients in the proportions required for certain polysilicates and disilicates of definite formulæ. These silicates, in a finely-powdered condition, were then shaken continuously for an hour with 1000 times their weight of dilute hydrochloric acid (0·25 per cent.), and the quantity of lead dissolved was determined by a colorimetric method depending on the comparison of the depth of tint with that given by known quantities of freshly produced lead sulphide.

The results may be thus stated:

(I.) *Influence of Alumina.*

	Polysilicates		Disilicates	
	(1)	(2)	(3)	(4)
SiO_2	28·8	35·1	35·1	41·9
PbO	71·2	60·9	64·9	54·5
Al_2O_3	—	4·0	—	3·6
	100·0	100·0	100·0	100·0
PbO dissolved	25	5	5	5 per cent.

No. 1 is the simple lead polysilicate $2PbO,3SiO_2 (=10PbO,15SiO_2)$, and No. 2 corresponds with the complex polysilicate

$$7PbO,Al_2O_3,15SiO_2;$$

thus the substitution in No. 2 of one molecule of Al_2O_3 for three molecules of PbO has had a very marked effect in decreasing the solubility of the lead.

No. 3 is the simple disilicate $PbO,2SiO_2 (=10PbO,20SiO_2)$, and No. 4 is the complex disilicate $7PbO,Al_2O_3,20SiO_2$. Here the substitution of Al_2O_3 for 3PbO has not affected the proportion of soluble lead, or at least, not sufficiently to be evident under the conditions of the experiment. A similar conclusion appears to have been arrived at recently by H. Eisenlohr (*Sprechsaal*, 1910, **43**, 389).

(II.) *Influence of Sodium Oxide.*

	Polysilicate (5)	Disilicate (6)
SiO_2	31·0	37·9
PbO	65·9	58·8
Na_2O	3·1	3·3
	100·0	100·0
PbO dissolved	44	13 per cent.

No. 5 is the polysilicate $2Na_2O,12PbO,21SiO_2$; it is to be compared with No. 1 ($=14PbO,21SiO_2$).

No. 6 is the disilicate $Na_2O,5PbO,12SiO_2$; its comparison sample is No. 3 ($=6PbO,12SiO_2$); thus in both cases the substitution of one molecule of Na_2O for one of PbO has materially increased the proportion of soluble lead.

(III.) *Influence of Alumina and Sodium Oxide Together.*

	Polysilicate (7)	Disilicate (8)
SiO_2	33·8	40·4
PbO	62·3	56·2
Al_2O_3	2·4	2·1
Na_2O	1·5	1·3
	100·0	100·0
PbO dissolved	8½	5 per cent.

No. 7 is the polysilicate $Na_2O,Al_2O_3,12PbO,24SiO_2$. It is to be compared with No. 1 and No. 2, also with No. 5. Relatively to No. 1, a considerable lowering of the proportion of soluble lead has been effected, and this, in accordance with (I) and (II), is to be attributed to the alumina. As compared with No. 2, a larger quantity of soluble lead is shown, in agreement with the fact that No. 7 contains a smaller percentage of alumina than No. 2.

No. 8 is the disilicate $Na_2O,Al_2O_3,12PbO,32SiO_2$. The proportion of soluble lead agrees with that in the simple disilicate No. 3.

(IV.) *Influence of Boron Trioxide.*

No borosilicates of definite molecular formulæ were made, but the following results were obtained with modifications of the simple disilicate:

	Disilicate	Modifications	
	(1)	(9)	(10)
SiO_2	35·1	30	35
PbO	64·9	65	60
B_2O_3	—	5	5
	100·0	100	100
PbO dissolved	5	53	46 per cent.

Thus the substitution of 5 per cent. of boron trioxide for the same quantity of either silica or lead oxide in the simple disilicate enormously increases the quantity of soluble lead. This effect, however, is not produced with the *complex* disilicates, or at least, not with those of a particular type. We had already noted (*loc. cit.*, p. 799) that from 4 to 6 per cent. of boron trioxide was present in certain borosilicates which yielded mere traces of lead to the action of solvents. But in these cases the proportion of silica was higher, and that of the lead oxide much lower, than in the two experiments above described, and notable quantities of lime and alumina were also present. Which of these factors determines the behaviour of the boron trioxide is at present obscure. It was precisely the influence of the various constituents that we had hoped to ascertain if the work had been completed.

The results obtained point clearly to the following conclusions:

(1) Alumina has a marked effect in promoting the stability of the polysilicates towards acids. Possibly this is due to its function in the silicate being that of an acidic oxide. In the disilicates this effect is less apparent, since these are already tolerably stable.

(2) Sodium oxide appears to increase the solubility of the lead, specially in the polysilicates.

(3) Boron trioxide in some cases renders the silicates much more easily attackable, but in others has no such effect.

Some experiments described by Beck, Löwe, and Stegmüller lead, in the main, to similar conclusions (*loc. cit.*, p. 214). With the simple lead silicates they mixed 2½ or 5 per cent. of one or other of the following compounds: Al_2O_3, B_2O_3, CaO, $Na_2B_4O_7$. The mixtures were fused, and the proportion of soluble lead was determined in the resulting complex silicates. Since by this procedure the acidity of the original silicates is modified, the results are not closely comparable with those that we adduce. Thus the addition of 5 per cent. of lime to the disilicate raised the percentage of soluble lead from 5·3 to 20·0; but this experiment is not analogous to those we show in (II) with sodium oxide, because the new compound is notably more basic than the original, and would therefore in any case be expected to yield more soluble lead. Nevertheless, the general results obtained point in the same direction as our own. Thus the effect of an addition of 5 per cent. of alumina could be traced in the decrease, by about 2 per cent., of the soluble lead in the disilicate (no experiments on the polysilicate are shown), and whilst 5 per cent. of borax raised the solubility figure of the disilicate from 5·3 to 32·0, the effect on the trisilicate was very slight, namely, an increase of only 1 per cent. Results of the same order were obtained with 5 per cent. of boron trioxide.

CCXL.—*The Colour and Absorption Spectra of Some Sulphur Compounds.*

By JOHN EDWARD PURVIS, HUMPHREY OWEN JONES, and HUBERT SANDERSON TASKER.

IN a previous paper (Jones and Tasker, Trans., 1909, **95**, 1904) the preparation and properties of some alkyl dithio-oxalates were described. These esters were found to exhibit a distinct yellow colour, whilst oxalates and oxalyl chloride are colourless.

The dithio-oxalates were found to have normal molecular weights in solution, so that it appears as if their colour had been produced owing to the replacement of oxygen by sulphur.

It was therefore decided to study the absorption spectra of these and some other sulphur compounds of similar structure in order to ascertain, if possible, the cause of the colour of thio-oxalates. The various ethyl and phenyl mono-, di- and tri-thiocarbonates were prepared and examined, as were also the corresponding dithio-oxalates, dithiomalonates, dithiosuccinates, and several other compounds containing two atoms of sulphur in the molecule. The results are described and discussed in this paper. We are not, at present, prepared to suggest a hypothesis to account for the results obtained; but those so far recorded for a number of coloured compounds of simple structure seem to be of value, and the publication of them may serve a useful purpose.

Each compound was obtained as pure as possible, its absorption spectrum studied in solution of various concentrations in pure ethyl alcohol, and the results are represented by curves in the usual way. A large number of the substances show no band due to selective absorption, and, in these cases, it will be sufficient if the reciprocals of the wave-lengths of the last transmitted lines at a thickness of 30 mm., and sometimes also of 2 mm., of solution be recorded; when the substance exhibits a band, the position of its head is also noted.

The following compounds were examined.

Thiocarbonates.

Diethyl thiocarbonate, OEt·CO·SEt, was prepared by the action of ethyl chlorocarbonate on sodium ethyl mercaptide (Salomon, *J. pr. Chem.*, 1873, [ii], **7**, 255).

Diethyl thioncarbonate, OEt·CS·OEt, was prepared as described by Debus (*Annalen*, 1850, **75**, 136), by the action of heat on ethyl xanthate, and was separated from the compound OEt·CS·SEt, which is formed at the same time, by repeated fractional distillation, until the product boiled between 161° and 161·5°.

Several analyses established the purity of the substance, which had a marked yellow colour. (For example: Found, S=23·9. $C_5H_{10}O_2S$ requires S=23·9 per cent.) We were not able to prepare this compound by the action of thiocarbonyl chloride on sodium or potassium ethoxide.

Diphenyl thioncarbonate, OPh·CS·OPh, was prepared by the action of thiocarbonyl chloride on aqueous sodium phenoxide (Bergreen, *Ber.*, 1888, **21**, 346; Eckenroth and Koch, *Ber.*, 1894, **27**, 1369).

The compound has been described as crystallising in colourless plates, but it was found that, after repeated recrystallisation from alcohol and other solvents, the compound still retained a very distinct cream colour. The colour was not intense, and small quantities of the substance might be taken to be colourless, whereas in large quantities the colour is unmistakable.

Diethyl dithiocarbonate, SEt·CO·SEt, was prepared by the action of carbonyl chloride on sodium ethylmercaptide (Salomon, *J. pr. Chem.*, 1872, [ii], **6**, 443).

Diphenyl dithiocarbonate, prepared by the action of carbonyl chloride on sodium thiophenoxide, crystallises from alcohol in long needles, melting at 43°, and is quite colourless.

Diethyl thionthiocarbonate, OEt·CS·SEt, prepared by the action of ethyl bromide on potassium xanthate (Salomon, *loc. cit.*, p. 445), shows a distinct yellow colour very similar to that of diethyl thioncarbonate.

Diethyl trithiocarbonate, prepared by the action of thiocarbonyl chloride on sodium ethylmercaptide, is a deep reddish-orange liquid, boiling at 240°/760 mm. and at 118—119°/10 mm. (Debus, *Annalen*, 1850, **75**, 147).

Diphenyl trithiocarbonate was prepared by the action of thiocarbonyl chloride on sodium thiophenoxide. It crystallises from alcohol in short prisms, melting at 43°, and showing a golden-yellow colour lighter than that of the ethyl compound:

0·1998 gave 0·4335 CO_2 and 0·0690 H_2O. C=59·2; H=3·84.

$C_{13}H_{10}S$ requires C=59·5; H=3·82 per cent.

Diethyl monothio-oxalate, prepared by the action of sodium ethylmercaptide on ethyl chloroglyoxylate ("chloroxalic ether"), as described by Morley and Saint (Trans., 1883, **43**, 400), is a liquid boiling at 216°, which shows a very pale yellow colour when examined in thick layers.

The various alkyl dithio-oxalates have already been described (Jones and Tasker, *loc. cit.*).

Diethyl dithiomalonate, prepared by the action of malonyl chloride on sodium ethylmercaptide, is a colourless liquid, boiling at 135°/10 mm. On distilling under atmospheric pressure, this ester appears to undergo decomposition with the formation of derivatives of ethyl mercaptan:

0·3421 gave 0·5443 CO_2 and 0·1894 H_2O. $C=43·4$; $H=6·15$.

$C_7H_{12}O_2S_2$ requires $C=43·8$; $H=6·25$ per cent.

Diphenyl dithiomalonate, prepared by the action of malonyl chloride on phenyl mercaptan or its lead salt, crystallises in long, colourless needles, melting at 94—94·5°:

0·2700 gave 0·6151 CO_2 and 0·1055 H_2O. $C=62·1$; $H=4·34$.

$C_{15}H_{12}O_2S_2$ requires $C=62·5$; $H=4·17$ per cent.

Diethyl dithiosuccinate, prepared by the action of succinyl chloride on sodium ethylmercaptide, is a colourless liquid, boiling at 165°/10 mm. The product when first formed was slightly fluorescent; the fluorescence persisted after distillation, but was removed by washing with dilute sodium hydroxide solution:

0·2355 gave 0·4010 CO_2 and 0·1465 H_2O. $C=46·4$; $H=6·91$.

$C_8H_{14}O_2S_2$ requires $C=46·6$; $H=6·8$ per cent.

Diphenyl dithiosuccinate, prepared by the action of succinyl chloride on phenyl mercaptan, crystallises from alcohol in colourless needles, melting at 90—90·5°:

0·1887 gave 0·4375 CO_2 and 0·0807 H_2O. $C=63·3$; $H=4·75$.

$C_{16}H_{14}O_2S_2$ requires $C=63·6$; $H=4·64$ per cent.

It may be mentioned that succinyl chloride, which is described as a liquid, when pure sets to a crystalline solid, melting at 17°.

Ethyl ethylthiolacetate, $SEt·CH_2·CO_2Et$, prepared from ethyl chloroacetate and sodium ethylmercaptide in the cold, is a colourless oil, boiling at 187—188° (Claesson, *Bull. Soc. chim.*, 1875, [ii], **23**, 445).

Ethyl ethylthiolthioacetate, $SEt·CH_2·CO·SEt$, was prepared by the action of chloroacetyl chloride on sodium ethylmercaptide; the reaction was started in a freezing mixture, and completed at 100°. The compound is a colourless liquid, boiling at 101—102°/5 mm.:

0·2163 gave 0·6095 $BaSO_4$. $S=38·7$.

$C_6H_{12}OS_2$ requires $S=39·0$ per cent.

s-*Diethylthiolethane*, $SEt{\cdot}CH_2{\cdot}CH_2{\cdot}SEt$, prepared by the action of ethylene dibromide on sodium ethylmercaptide at 100°, is a colourless liquid, boiling at 210° (Ewerlöf, *Ber.*, 1871, **4**, 717; Meyer, *Ber.*, 1886, **19**, 3266).

Phenyl mercaptan was obtained from Kahlbaum, and thiocarbonyl chloride from Schuchardt; both were purified by distillation. Diphenyl disulphide was prepared and purified by repeated crystallisation until quite colourless.

We are indebted to Professor Pope for a specimen of pure benzyl sulphide.

Carbonates.

An examination of the absorption curves (Figs. 1 and 2) shows that well-marked bands are exhibited by diethyl dithio- and trithiocarbonates (*M*/1000-solutions), a less pronounced band by diethyl thioncarbonate (*M*/100-solution) and by diphenyl carbonate and dithiocarbonate (*M*/1000-solutions), and by diphenyl thion- and trithio-carbonates (*M*/10,000-solutions). Table I gives the limits of general absorption in oscillation frequencies at a thickness of 30 mm., and, when stated, also at 2 mm.; the position of the head of the absorption band, when one is present, is also given.

TABLE I.

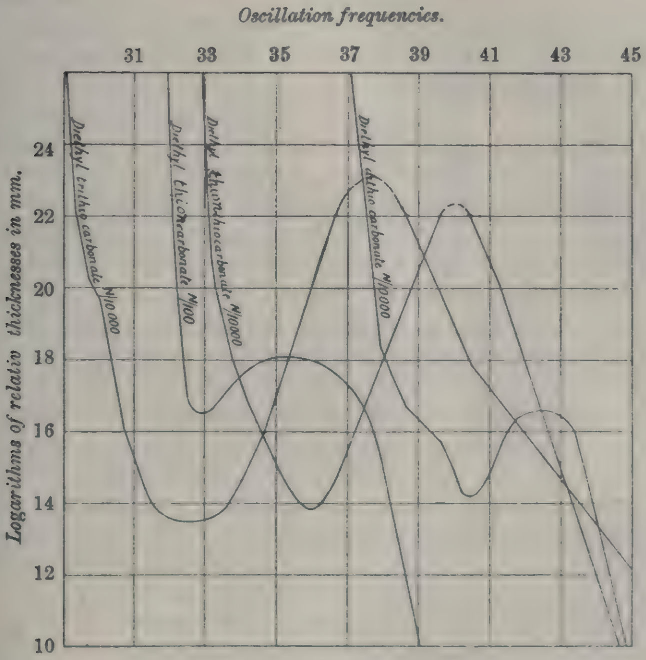
Substance.	Strength of solution.	Head of band.	Limit of absorption.
$CO(OEt)_2$ (colourless)	*M*/10	—	4406
	M/10 (2 mm.)	—	4620
$CO(OPh)_2$,,	*M*/100	—	3575
$CO(OPh)_2$,,	*M*/1000	3760	3584
$CO(OEt)(SEt)$ (colourless)	*M*/10	—	3435
	M/10 (2 mm.)	—	4173
$CO(OEt)(SEt)$,,	*M*/1000	—	4254
$CS(OEt)_2$ (yellow)	*M*/10	—	3047
	M/100	3280	—
$CS(OEt)_2$,,	*M*/10,000	—	3980
$CS(OPh)_2$ (cream coloured)	*M*/100	—	3336
$CS(OPh)_2$,,	*M*/1000	3660	3453
$CO(SEt)_2$ (colourless)	*M*/100	—	3513
$CO(SEt)_2$,,	*M*/10,000	4058	3722
$CO(SPh)_2$,,	*M*/1000	—	3405
$CS(OEt)(SEt)$ (yellow)	*M*/100	—	3173
$CS(OEt)(SEt)$,,	*M*/1000	3600	—
$CS(SEt)_2$ (orange)	*M*/100	—	2801
$CS(SEt)_2$,,	*M*/10,000	3260	—
$CS(SPh)_2$ (golden-yellow)	*M*/100	—	2695
$CS(SPh)_2$,,	*M*/10,000	3300	3030
$CSCl_2$ (orange-red)	*M*/10	—	3010
	M/1000	—	3508

The results given above show that in general the replacement of an ethyl by a phenyl group causes a shift in the limit of general absorption towards the red end of the spectrum.

Further, the replacement of oxygen by sulphur in ethyl carbonate and ethyl thioncarbonate causes a very marked increase in the absorption.

The consideration of the cause of the colour and bands exhibited by these compounds is complicated by the differences which exist between the ethyl and phenyl esters. Diethyl carbonate shows merely general absorption but no band, whilst diphenyl carbonate shows a well-defined band (Fig. 2), with its head about 3740, (oscillation frequency) almost identical in position with that of phenol. This band may therefore be attributed to the presence of the phenyl groups, the group $O:C<^{O\cdot}_{O\cdot}$ having no tendency to produce a band. This is the only case in which the modification of the curve by the substitution of phenyl for ethyl is in the direction of band formation; usually a band shown by the ethyl ester is partly and completely obliterated in the phenyl ester, as, for instance, in the dithiocarbonate and in the dithio-oxalate, which will be discussed

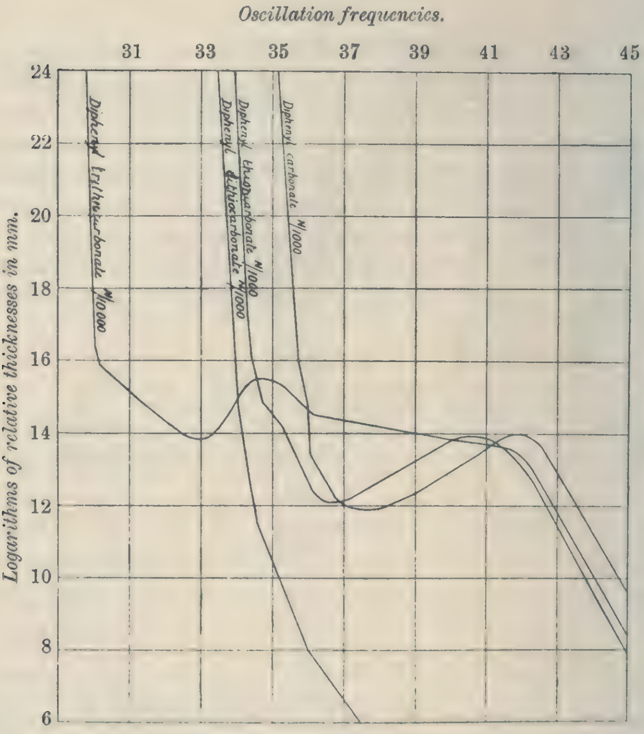
FIG. 1.



later. In the compound $CS(OPh)_2$, the band shown by diphenyl carbonate has been displaced slightly towards the red end of the spectrum, whilst in diphenyl trithiocarbonate the band is so changed that its form suggests a compromise between the vibration due to the phenyl groups, and those due to the group $S\colon C<\begin{matrix}S\cdot\\ S\cdot\end{matrix}$, which produce the band found in diethyl trithiocarbonate.

In consequence of these complications introduced by the presence of phenyl groups, the curves of the ethyl esters only can be considered completely comparable with one another. Considering first the phenomenon of colour, it is obvious that the mere replacement of one or two oxygen atoms by sulphur does not give rise to colour, since diethyl and diphenyl dithiocarbonates are colourless; but it is also clear that the group $\colon C\colon S$ must be regarded as a powerful chromophore.

FIG. 2.



The following compounds all exhibit colour which may be regarded as caused primarily by the $\colon C\colon S$ group: $CSCl_2$ (orange-red), $CS(OEt)_2$

(yellow), $CS(OPh)_2$ (cream), thiobenzophenone, $CS(Ph)_2$ (blue). In the case of thiobenzophenone and dimethoxythiobenzophenone, we have confirmed the results obtained by Gattermann (*Ber.*, 1895, **28**, 2868) as regards the properties of the compounds and the fact that their molecular weights in solution are normal. We have also been able to prepare these compounds by the interaction of dry silver sulphide and the corresponding chloride. The colour originating in the $\vdots C \vdots S$ group is very considerably modified by the group to which it is attached, since in the cases mentioned above it varies from deep blue to cream.

The difference between the intensity of the colour exhibited by the compounds $CS(OEt)_2$ and $CS(OPh)_2$ is much more marked than that between diacetyl and benzil, but the explanation is possibly similar to that suggested by Baly and Stewart (Trans., 1906, **89**, 502) to meet the case of these substances.

Until there is more exact knowledge as to the relation between the absorption of light and the structure of organic compounds, it is not desirable to formulate further hypotheses, but the striking difference between the groups $\vdots C \vdots S$ and $\vdots C \vdots O$ may be explained as suggested by Hewitt at the International Congress of Applied Chemistry, 1909, on the following consideration. The attraction between carbon and sulphur is less than that between carbon and oxygen, as evidenced by the ease with which the sulphur is replaced by oxygen in the thioketones, thioncarbonates, and thiocarbamides. The mass of the sulphur atom to be held by the smaller force of attraction is greater, and consequently the period of any vibration set up would be slower.

The bands exhibited by the three compounds $CO(SEt)_2$, $CS(OEt)(SEt)$, and $CS(SEt)_2$ possess a similar shape and persistency, but are shifted successively towards the red end of the spectrum, and become much broader. It is possible that these bands may arise owing to the formation of linkings between the sulphur atoms, which exhibit a greater tendency to become quadrivalent than does oxygen.

Oxalates.

Table II gives, for the oxalates and thio-oxalates, the strength of solution, position of head of band in oscillation frequency, and the limit of absorption through 30 mm. of solution.

Fig. 3 contains the curves for those substances which show bands.

TABLE II.

Substance.	Strength of solution.	Head of band.	Limit of absorption.
$(CO_2Et)_2$ (colourless)	M/10	—	3513
$(CO_2Et)_2$,,	M/1000	—	4423
$(CO_2Ph)_2$,,	M/100	Rapid extension of absorption between 3640 and 4000, indicating potential band.	3400
$(CO_2Ph)_2$,,	M/10,000		3593
$CO_2Et·CO·SEt$ (almost colourless)	M/10	—	2770
$CO_2Et·CO·SEt$,,	M/1000	3740	3320
$(CO·SEt)_2$ (yellow)	M/10	—	2468
$(CO·SEt)_2$,,	M/1000	3640	3144
$(CO·S·C_3H_7)_2$,,	M/10	—	2484
$(CO·S·C_3H_7)_2$,,	M/1000	3620	3038
$(CO·SPh)_2$,,	M/100	—	2380
$(CO·SPh)_2$,,	M/1000	Rapid extension of absorption between 3110 and 3850.	3050

Table III gives similar data, including the limit of absorption for a thickness of 2 mm. of solution, for the thiomalonates and other compounds examined, which are all colourless, and none of which show bands.

TABLE III.

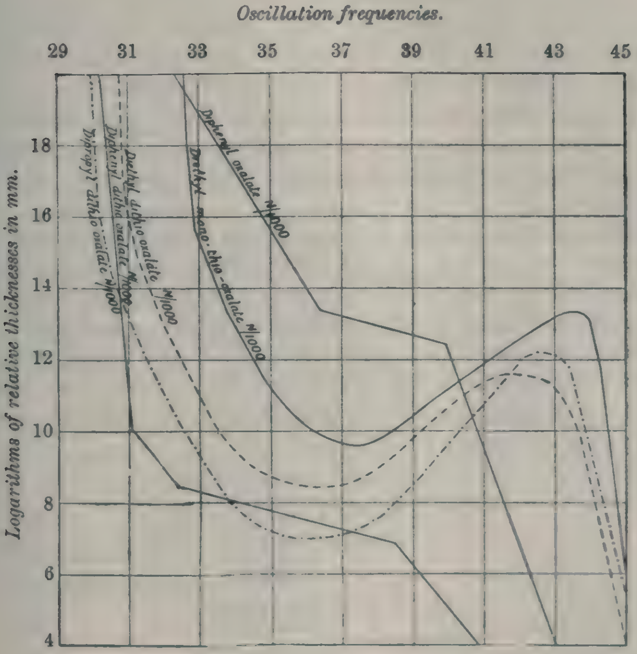
Substance.	Strength of solution.	Limit of absorption.
$CH_2(CO·SEt)_2$	M/1000	3727
	M/1000 (2 mm.)	4063
$CH_2(CO·SPh)_2$	M/1000	3405
	M/1000 (2 mm.)	4005
$(CH_2·CO·SEt)_2$	M/1000	3855
	M/1000 (2 mm.)	4199
$(CH_2·CO·SPh)_2$	M/1000	3447
	M/1000 (2 mm.)	4005
$(CH_2·SEt)_2$	M/1000	4365
	M/1000 (2 mm.)	4603
$SEt·CH_2·CO_2Et$	M/1000	4354
	M/1000 (2 mm.)	4422
$SEt·CH_2·CO·SEt$	M/1000	3830
	M/1000 (2 mm.)	4113

In all the above cases, the replacement of oxygen by sulphur produces a very great increase in the absorptive power of the compound; this is particularly well illustrated by a comparison of ethyl oxalate and monothio-oxalate (table II) and of the two last compounds in table III.

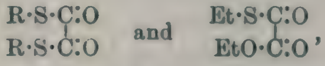
In the colourless compounds, the replacement of ethyl by phenyl produces a considerable increase in absorption, but this is not so marked in the coloured compounds, since in the dithio-oxalate the absorptive power of the phenyl compound is intermediate between those of the ethyl and propyl compounds.

The potential band exhibited by phenyl oxalate is probably due to the phenyl groups, as in the case of phenyl carbonate, since its position is close to that of the phenol band.

FIG. 3.



The table and the curves show that both colour and an absorption band are produced by the structures:



$$\begin{array}{l} R\cdot S\cdot C\colon O \\ \quad\;\; | \\ R\cdot S\cdot C\colon O \end{array} \quad \text{and} \quad \begin{array}{l} Et\cdot S\cdot C\colon O \\ \qquad\;\; | \\ EtO\cdot C\colon O \end{array},$$

but when R = Ph the band is almost obliterated, as in the case of the dithiocarbonate. Neither colour nor band is shown by any of the other compounds which were examined containing two atoms of sulphur in the molecule. It may therefore be concluded that the above structure is associated with the existence of the colour and the band.

Colour of Oxalyl Chloride in Solution.

It was observed that, although oxalyl chloride itself and its solutions in substances like ether, chloroform, and paraffins were quite colourless, yet it forms yellow solutions with phenol, anisole, piperonal, dipentene, and alkyl sulphides. The colour of these solutions is similar to, but deeper than, that of the alkyl dithiooxalates, but the solutions were too unstable to allow of an examination of their spectra.

Oxalyl chloride therefore forms coloured solutions with certain substances which also give coloured solutions with tetranitromethane (Werner, *Ber.*, 1909, **42**, 4324). The production of colour from oxalyl chloride by admixture with other substances is possibly due to the formation of additive products with these substances, which, in virtue of the presence of oxygen, sulphur, or ethenoid linkings in the molecule, are capable of forming such additive compounds.

Much further work will be required before definite hypotheses can be formulated to account for the behaviour of these sulphur compounds, and it is hoped that the study may be continued and possibly extended to some corresponding selenium compounds.

The absorption spectra of phenyl mercaptan and benzyl sulphide have also been examined for comparison with phenol and benzyl alcohol. These substances show no band, and the limits of absorption are given in table IV.

TABLE IV.

Substance.	Strength of solution.	Limit of absorption.
$C_6H_5{\cdot}SH$	*M*/100 (30 mm.)	3320
	M/1000 (30 mm.)	3460
$(C_6H_5{\cdot}CH_2)_2S$	*M*/100 (30 mm.)	3532
	M/1000 (30 mm.)	3608

It is remarkable that the pronounced band in phenol has been completely obliterated by the replacement of oxygen by sulphur, and that the three bands in benzyl alcohol (Baly and Collie, Trans., 1905, **87**, 1332) have disappeared in benzyl sulphide.

The results obtained in the examination of benzyl mercaptan are not trustworthy on account of the ease with which it is oxidised in solution.

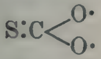
The obliteration of bands is possibly to be attributed to the greater absorptive power of the sulphur compounds.

General Results.

An examination of the absorption spectra of sulphur compounds has shown that:

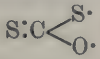
(1) The replacement of oxygen by sulphur causes a marked increase in the absorptive power of the compound, and, indeed, often results in the production of colour. An absorption band also appears in some cases.

(2) Definite absorption bands are shown by sulphur compounds possessing the following structures, but are not shown by the corresponding oxygen compounds:



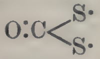
$\mathrm{S{:}C}<\!\begin{matrix}\mathrm{O\cdot}\\ \mathrm{O\cdot}\end{matrix}$

(I.)



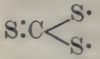
$\mathrm{S{:}C}<\!\begin{matrix}\mathrm{S\cdot}\\ \mathrm{O\cdot}\end{matrix}$

(II.)



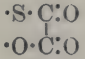
$\mathrm{O{:}C}<\!\begin{matrix}\mathrm{S\cdot}\\ \mathrm{S\cdot}\end{matrix}$

(III.)



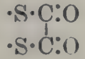
$\mathrm{S{:}C}<\!\begin{matrix}\mathrm{S\cdot}\\ \mathrm{S\cdot}\end{matrix}$

(IV.)



$\begin{matrix}\mathrm{\cdot S\cdot C{:}O}\\ |\\ \mathrm{\cdot O\cdot C{:}O}\end{matrix}$

(V.)



$\begin{matrix}\mathrm{\cdot S\cdot C{:}O}\\ |\\ \mathrm{\cdot S\cdot C{:}O}\end{matrix}$

(VI.)

Of these, compounds of the type I, II, IV, and VI are yellow in colour, and V may be considered as faintly coloured.

(3) The group $\mathrm{S{:}C}<$ must be considered a powerful chromophore.

(4) In certain aromatic compounds, such as phenol and benzyl alcohol, the replacement of oxygen by sulphur results in obliterating absorption bands.

(5) It has also been found that, although oxalyl chloride itself is colourless, it gives yellow solutions with a number of unsaturated compounds and compounds containing oxygen or sulphur.

The expenses of this work were largely defrayed by grants from the Government Grant Committee of the Royal Society, and the spectra were examined by means of a spectroscope kindly placed at our disposal by the same body. For both these favours we are glad to make this grateful acknowledgment.

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CCXLI.—*Phenomena Observed when Potassium Mercuri-iodide is Dissolved in Ether and Water.*

By JAMES ERNEST MARSH.

POTASSIUM mercuri-iodide, $\mathrm{KHgI_3,H_2O}$, crystallises well from alcohol, but is decomposed by water with separation of mercuric iodide. A crystal of the salt changes in colour from yellow to red on being moistened with water. The salt is, however, soluble in water if heated with a very small quantity; also, when heated in a sealed tube, the dry salt melts at 119°, and this liquid may be regarded as a solution of the salt in its water of crystallisation. The salt is very sparingly soluble in dry ether, but is somewhat readily dissolved by undried ether, especially by ether which has been shaken with water and then separated from the latter. The salt, which dissolves in the ether with considerable rise of temperature, is much more soluble in cold ether than in hot. The following experiment illustrates this property. A sealed tube was employed containing 3·32 grams of powdered potassium iodide and 9·08 grams of mercuric iodide with 52 c.c. of "wet" ether and 0·6 c.c. of water. At 0° the contents of the tube are completely dissolved. If the tube is now placed in warm water, crystals begin to form, and at 50° the contents of the tube become nearly solid, with the formation of long, yellow needles of the salt $KHgI_3,H_2O$. The crystals redissolve in the ether on cooling. Analysis of the salt obtained in this way gave:

Found, $H_2O = 2·69$; $KI = 25·7$.

$KHgI_3,H_2O$ requires $H_2O = 2·82$; $KI = 26·0$ per cent.

If potassium iodide and mercuric iodide are mixed with ordinary undried ether, no apparent solution or other change occurs. The red and the colourless salts remain unchanged in presence of the solvent. After many weeks, however, the red colour of the mercuric iodide begins to fade, and its place is taken by the characteristic yellow, crystalline double salt. This does not dissolve appreciably in the ether now deprived of its water, but requires "wet" ether for its solution.

When potassium iodide and mercuric iodide are mixed with ether dried either by sodium or by long keeping over calcium chloride, the double salt which contains water of crystallisation cannot now be formed, and a quite different action occurs. The two salts rapidly liquefy in the ether, and take up four molecules of ether to form a heavy, yellow liquid compound. If any excess of ether is taken, it is left floating on the surface as a separate layer which contains very little of the salts, and a large excess of ether does not appreciably diminish or increase the volume of the liquid compound. If the ether taken is not enough to supply four molecules, then some of the salts are left undissolved. If mercuric iodide is taken in larger quantity than one molecule to one of potassium iodide, the excess is left undissolved.

The compound, $KHgI_3,4Et_2O$.—1·66 Grams of well powdered and dried potassium iodide and 4·54 grams of mercuric iodide were mixed with 4·4 c.c. of dry ether in a sealed tube. On shaking, all rapidly passed into solution. The liquid compound measured 5 c.c., and the ethereal layer 0·1 c.c., at 7·5°. From these figures the formula of the liquid compound and its specific gravity, 1·87, at 7·5° are derived. It should be noted that the solubility of potassium iodide and of mercuric iodide separately in dry ether is very slight. The solubility of potassium iodide in ether at the ordinary temperature was found to be 0·016 per cent., and of mercuric iodide 0·3 per cent., and in neither case is there formed any liquid not miscible with ether. The liquid compound of ether and potassium mercuri-iodide is also formed by exposing a mixture of the two salts in a tube to the vapour of ether, but in this case some crystals are also formed in the tube, and the action is very slow. 0·83 Gram (1 mol.) of potassium iodide and 2·27 grams (1 mol.) of mercuric iodide exposed to the vapour of dry ether increased in weight by 1·1682 grams (3·1 molecules of ether), when the red mercuric iodide just dissolved, and gave a further increase, in all, 1·5334 grams (4·1 molecules of ether), after keeping for many days. The compound was also analysed by determining the loss of weight due to the ether given off on passing a stream of dry air over the substance. The liquid, when it had lost a certain quantity of ether, began to crystallise, and soon formed a solid mass of crystals. It was then weighed, and the stream of air was continued until all the ether was expelled. 4·2914 Grams of the liquid compound gave 3·7086 grams of crystals, and finally 2·6314 grams of potassium and mercuric iodides. These numbers agree with four molecules of ether in the liquid compound, and with 2·5 molecules in the crystalline compound. As it is difficult to stop when the crystals are just free from liquid, it appears more probable that the crystalline compound is represented by the formula $KHgI_3,3Et_2O$.

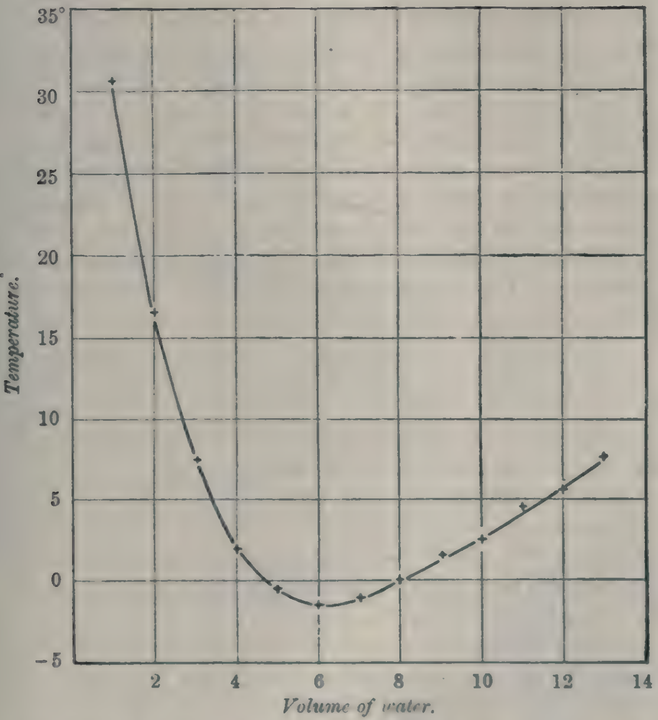
When the liquid compound is exposed to moist air, crystals of the hydrated salt $KHgI_3,H_2O$ at once form on the sides of the tube. The addition of a small quantity of water causes the liquid to set to an almost solid mass of crystals with total expulsion of the ether. The experiment was carried out as follows.

In a tube, containing 1·83 grams of potassium iodide, 5·0 grams of mercuric iodide, and 5 c.c. of dry ether, was placed a sealed bulb containing 0·22 gram of water, and a small piece of glass rod. The tube was then sealed, and, on mixing carefully so as not to break the bulb, the liquid compound was obtained with a small surface layer of ether. The bulb was then broken by a jerk, and the tube quickly became filled with a mass of yellow crystals insoluble in the ether.

Solution of Potassium Iodide and Mercuric Iodide in a Mixture of Ether and Water.—As stated above, the addition of water to the compound $KHgI_3,4Et_2O$ causes the precipitation of the salt $KHgI_3,H_2O$, and on the further addition of water the crystals become soluble in aqueous ether, to separate again on warming the solution. By continuing the addition of water, these crystals no longer separate on warming, nor does the water cause the separation of ether, but eventually red mercuric iodide is precipitated. This occurs when the amount of water added is just double the volume of the ether; the addition of a little more ether clears the solution. With a larger amount of ether than four molecules to one of the salts, the addition of water may cause the liquid to separate into two layers. When there is separation, it is found that there is a temperature, the critical point, below which complete mixture takes place, and above which there is a separation into layers. This critical temperature depends on the concentration of the double salt in solution and the relative amounts of ether and water. It is to be noted further that, whereas the addition of water to the mixture of potassium and mercuric iodides brings about partial solution with absorption of heat, the addition of ether brings about complete solution with evolution of heat, and the further addition of the water to the aqueous ethereal solution also causes an evolution of heat. The following example shows the effect of increasing quantities of water, the amounts of potassium iodide, mercuric iodide, and ether being constant. One molecular proportion of potassium iodide and one of mercuric iodide were mixed with 12·5 molecular proportions of water; the temperature fell 2°, the solution not being complete. On addition of 12·5 molecular proportions of ether, the temperature rose 10°, the solution being now complete. The critical point of this solution was 31°. Successive additions of 12·5 molecular proportions of water were made, and a rise of temperature in each case was noticed until it became too small to be measured. The critical point was determined after each addition of water. The results are illustrated by the curve in Fig. 1. It will be seen that the critical point falls to a minimum and rises again. It was found that the solution of lowest critical point froze when the temperature was reduced to about $-15°$. The composition of the liquid of lowest critical point, and therefore also of the frozen mass, is represented nearly by the rather complex formula $KHgI_3,12·5Et_2O,75H_2O$. The volume relations are more simple, being nearly 1 vol. $KHgI_3$: 3 vols. Et_2O : 3 vols. H_2O. When partly melted and no longer adhering to the sides of the tube, the solid mass floats on the surface of the liquefied part.

There is a further point to be noted with regard to the critical point. It is found that, when the most concentrated solution, namely, that which has the critical point of 31°, is heated, a heavy liquid layer separates at the bottom of the tube, increasing in amount as the temperature rises, and being redissolved as the temperature falls, until at 31° it disappears altogether. On the other hand, all the other solutions, when heated above their critical points, expel a light layer, which increases with the temperature and is re-absorbed by the bulk of the liquid just below the critical point. It will thus be seen that a solution of one molecular proportion of potassium mercuri-iodide in 12·5 molecular proportions of ether and 12·5 of water expels, on warming, a heavy liquid layer, whereas a solution containing the same quantities with an addition of 12·5 molecular proportions or more of water expels, on warming, a light liquid layer. If, now, we take an intermediate amount of water, namely, 18·75 molecular proportions, the other quantities remaining the same, a solution is obtained which, on warming, expels both a heavy liquid layer and a light one, so that three different liquids appear in the tube. In one experiment a sealed tube was used which contained 5·53 grams of potassium iodide, 15·1 grams of mercuric iodide, 10 c.c. of water, and 44·2 c.c. of "wet" ether. This solution is homogeneous at the ordinary temperature, and between 50° and 60° a good separation is obtained

FIG. 1.

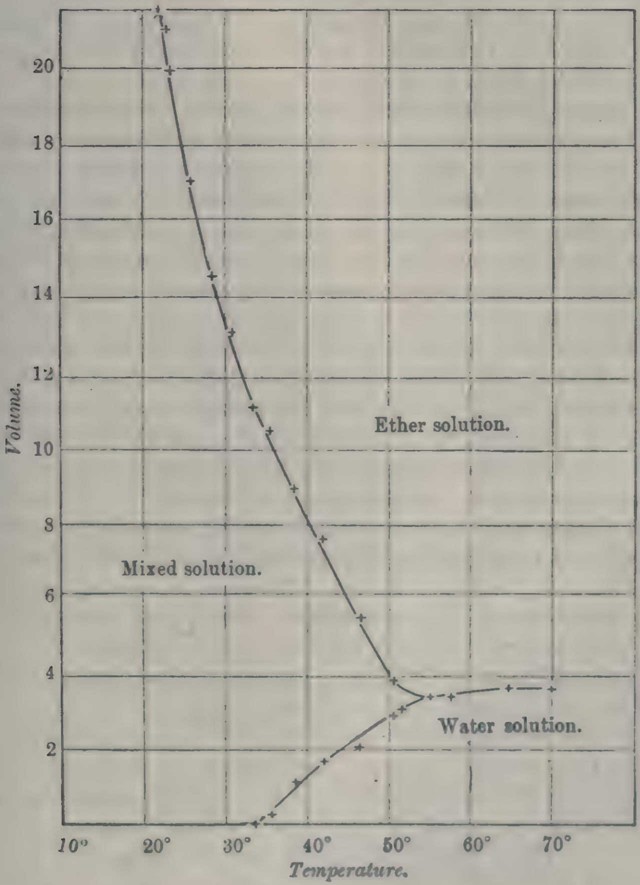


into three liquid layers. These layers are permanent and not altered by shaking while the liquid is still hot, but on cooling they form again a homogeneous solution.

It is possible to obtain other solutions which, on heating, give three liquid layers and have concentrations different from that just mentioned. The one which was first obtained contained equal molecular proportions of water and ether. As has already been stated, with the concentration of 1 to 12·5, a lower layer begins to separate at 31°; with the concentration of 1 molecular proportion of salt to 25 molecular proportions of ether and 25 of water, the upper layer separates above the critical point 0°. By trying concentrations between these two limits, it was found that with the concentration of 1 molecular proportion of potassium mercuri-iodide to 17·3 molecular proportions of water and 17·3 of ether, the solution separated into three layers. In a calibrated tube, 1·66 grams of potassium iodide, 4·54 grams of mercuric iodide, 2·6 c.c. of water, and 18·2 c.c. of "wet" ether were sealed. The calculated volume of the constituents is 22·0 c.c. The volume found on mixing was 21·4 c.c., so that there was a slight contraction. The tube was then heated to different temperatures, and the volumes of the solutions were determined. The curve plotted from the measurements is given in Fig. 2. In what follows, the top layer is termed "ether" solution, the middle layer "mixed" solution, and the lower layer "water" solution. At 22°, "ether" solution begins to separate, and increases in amount as the temperature rises. At 33·5°, "water" solution also begins to separate, and both layers increase with the temperature. At 51·5°, the "mixed" solution disappears, and only two liquids are present. These two liquids do not appreciably alter in volume on heating further to above 70°. Correction was made for expansion by heat, which was regular, and nearly the same as the expansion of ether itself. In order to determine the amounts of mercuric iodide and potassium iodide in the water layer, a tube was taken with a bulb of 4 c.c. capacity at one end, the mixture in the tube being made up of 2 molecular proportions of potassium mercuri-iodide (12·4 grams) to 25 of ether and water. On heating, the heavy aqueous solution just filled the bulb at 63°. The tube was cooled without mixing the two solutions, opened, and the solutions separated. The aqueous solution measured slightly less than 4 c.c. The mixed salts contained in it weighed 4·77 grams, of which 1·58 grams was potassium iodide. The solution contained scarcely any ether, it did not take fire (water containing 0·5 per cent. of ether takes fire), and had scarcely any odour of ether. It was thus found that an aqueous-ethereal solution of the salts, which is homogeneous when cold, separates, on warming, into a "water" solution nearly free from ether, and an "ether" solution which, from the volumes of the two solutions, can contain but little water.

In order to determine how the mercuric and potassium iodides are apportioned in all the three layers, a solution was made which gave three layers at a temperature below the boiling point of ether.

FIG. 2.



The three layers can then be produced in a stoppered burette, and run off and analysed. It was found that with 1 molecular proportion of salt to 20 molecular proportions of water and 33 of ether, a separation into three layers is obtained at 29°. The "water" layer measured 0·6 c.c., had a concentration of 1 gram per c.c., and contained $HgI_2 : KI = 2 : 3$ mols. The "middle" layer measured

6·2 c.c., had a concentration of 0·4 gram per c.c., and contained HgI_2 : KI = 1 : 1 mol. The "ether" layer measured 31 c.c., had a concentration of 0·1 gram per c.c., and contained HgI_2 : KI = 7 : 6 mols.

It will be noticed that the "water" solution contains more, and the "ether" solution less, potassium iodide than is represented by the simple molecular proportions HgI_2 : KI. It was found that "wet" ether will dissolve mercuric iodide and potassium iodide in any proportions between the lower limit KI : HgI_2 and the upper limit KI : $2HgI_2$. The upper limit of solubility of water is KI : HgI_2, whilst there is, of course, no lower limit.

There seems no doubt that this separation of a homogeneous solution into layers on warming is associated with the temperature changes which occur on making the solutions. There are four operations, three of which occur with evolution of heat, and one with absorption of heat. In the first place, mercuric iodide and potassium iodide together dissolve in water with absorption of heat. The same salts dissolve in ether with evolution of heat. Further, ether dissolves in the "water" solution with evolution of heat, and water also dissolves in the "ether" solution of the salts with evolution of heat. It would be expected that the effect of raising the temperature would be to assist the change which occurs with absorption of heat, and to prevent those changes which occur with evolution of heat. Thus either ether will be expelled from solution, which happens at low concentrations, or water will be expelled, which happens at high concentrations, or both ether and water will be expelled, and further the salts will be expelled from the "ether" solution into the "water" solution. There is thus eventually produced, at a sufficiently high temperature, a strong aqueous solution, together with a weak ethereal solution of the two salts. These changes are reversed on cooling. If not shaken, however, the solutions may be kept apart when cooled; they mix then on shaking without change of temperature or volume. The great concentration of salts in the "water" layer is well shown by heating a tube, containing 1 molecular proportion of salt to 12·5 molecular proportions of water, to about 70°, and then, without shaking, cooling rapidly to 0°. The "water" layer now becomes filled with crystals of the double salt mixed with the red crystals of mercuric iodide.

Compounds of Two Haloid Salts with Ether.

A number of compounds analogous to the compound $KHgI_3,4Et_2O$ were also prepared. The alkali-metal iodides form liquid compounds with mercuric iodide and ether, with the exception of rubidium and cæsium iodides. The compounds obtained have the following formulæ:

$$NaI,HgI_2,6Et_2O$$
$$KI,HgI_2,4Et_2O$$

$LiI,HgI_2,6Et_2O$	$LiBr,HgI_2,4Et_2O$	$[LiCl,HgI_2\ ?]$
$LiI,HgBr_2,5Et_2O$	$LiBr,HgBr_2,4Et_2O$	$LiCl,HgBr_2,Et_2O\ ?$
$[LiI,HgCl_2\ ?]$	$LiBr,HgCl_2,Et_2O\ ?$	$[LiCl,HgCl_2\ ?]$

$LiI,AgI,3Et_2O$
$LiI,CuI,4Et_2O$

The compound $KI,HgI_2,4Et_2O$ is described on p. 2298. The amount of ether (4 molecules) is approximately correct at the ordinary temperature, but the compound is affected by a rise of temperature with loss of some of the ether. This effect is found to be a general one for this class of substances even when they are contained in sealed tubes; it is small in the case of the lithium and sodium mercuri-iodides. The experiments which are now to be described are not therefore intended to furnish accurate analytical data, but rather to show how the substances were obtained. They indicate also that the constituents are combined at the ordinary temperature in approximately simple molecular proportions, the amount of the solvent being limited to six molecules or less. The liquids can, however, hardly be regarded as "definite" compounds in the ordinary sense, nor are they ordinary solutions, since they are saturated both for salt and for solvent. They seem to be of a nature intermediate between a solution and a chemical compound.

Compounds of Iodides with Mercuric Iodide and Ether.

Lithium Iodide.—Lithium iodide alone is readily soluble in dry ether, although not in undried and "wet" ether. It does not, however, form a liquid compound with a limited amount of ether in presence of excess of ether.

1·4 Grams of lithium iodide and 5·05 grams of mercuric iodide were mixed in a stoppered burette with 10 c.c. of dry ether, when all dissolved rapidly, forming two liquid layers. The volume of the solution was 8·15 c.c., and that of the upper ether layer 2·55 c.c. The latter left, on evaporation, 0·015 gram of solid residue, consisting of lithium mercuri-iodide, $LiHgI_3$. Hence the liquid compound contained 1·387 grams of lithium iodide, 5·038 grams of mercuric iodide, and 7·45 c.c. of ether in 8·15 c.c. From these numbers is derived the formula $LiI,HgI_2,6Et_2O$, and the specific gravity 1·461

Sodium Iodide.—1·53 Grams of sodium iodide and 3·67 grams of mercuric iodide were sealed in a tube with 6 c.c. of dry ether. The contents of the tube liquefied readily on shaking, with the exception of some sodium iodide, of which excess was taken by accident. The ether not required was 0·8 c.c. The formula of the compound formed is $NaI,HgI_2,6Et_2O$.

Rubidium Iodide.—Rubidium iodide and mercuric iodide in contact with dry ether gave no liquid compound. There is no apparent action at first, but after some days the red mercuric iodide disappears, and its place is taken by a yellow, crystalline substance.

Caesium Iodide.—Cæsium iodide and mercuric iodide gave no liquid compound with ether, and after several months most of the mercuric iodide appeared to be unchanged.

Silver Iodide.—Silver iodide and mercuric iodide in ether do not appear to suffer any change.

Strontium Iodide.—1·44 Grams of strontium iodide and 3·67 grams of mercuric iodide, with 6 c.c. of dry ether, liquefied and combined with 2·63 c.c. of the ether; hence the formula of the liquid compound is $SrI_2,2HgI_2,6Et_2O$.

Aluminium Iodide.—Aluminium iodide and mercuric iodide did not give any liquid compound with ether, but the colour of the mercuric iodide disappeared with the formation of a yellow precipitate and, after a time, of large, colourless crystals.

Hydrogen Iodide.—1·27 Grams of mercuric iodide were mixed with 3 c.c. of dry ether, and dry hydrogen iodide was passed in until the mercuric iodide just dissolved. Two layers of liquid were formed, and the upper layer of unused ether measured 2·25 c.c. The probable formula of the compound is $HI,HgI_2,3Et_2O$.

Tetramethylammonium Iodide.—Tetramethylammonium iodide and mercuric iodide suffer no apparent change in dry ether after several months.

Ammonium Iodide.—The compound of ammonium iodide and mercuric iodide with ether differs from the other compounds described, in that its composition is different at different temperatures. 0·584 Gram of ammonium iodide and 1·83 grams of mercuric iodide, with 3 c.c. of dry ether, gave two liquids, the unused ether measuring 0·8 c.c. This agrees with the formula $NH_4I,HgI_2,5Et_2O$. At about 80°, 1 molecule of ether is expelled from the lower to the upper layer in the sealed tube. Thus the compound $NH_4I,HgI_2,4Et_2O$ is left.

If water is added to ammonium and mercuric iodides dissolved in excess of ether, no crystalline hydrate separates, but the water is absorbed to a certain amount, and then any excess of water remains undissolved as a light layer floating on the heavy ether solution. The water layer contains very little of the salt dissolved.

Compounds of Bromides with Mercuric Bromide and Ether.

Lithium Bromide.—0·4 Gram of lithium bromide and 1·8 grams of mercuric bromide were sealed in a tube with 3 c.c. of dry ether. The mixture readily liquefied, and formed two layers. The amount of ether in excess was 1·02 c.c., hence the formula of the liquid compound is $LiBr,HgBr_2,4Et_2O$.

Sodium Bromide.—Sodium bromide and mercuric bromide gave no liquid compound with ether.

Ammonium Bromide.—1·43 Grams of ammonium bromide and 5·3 grams of mercuric bromide were sealed in a tube with 5·5 c.c. of ether. The salts liquefied, but not quite completely, and required 3·66 c.c. of ether. This agrees with the formula

$$NH_4Br,HgBr_2,2{\cdot}5Et_2O.$$

This compound, however, like the corresponding iodide, loses ether when warmed in the sealed tube, leaving not another liquid compound, but a solid mass, with loss of probably all the ether. The mass slowly unites again with the ether when cold. Further, when the liquid compound itself is cooled to about 10°, it sets to a solid mass of colourless crystals without any loss of ether.

Lithium Chloride and Mercuric Chloride.

0·42 Gram of lithium chloride and 2·71 grams of mercuric chloride were sealed with 3 c.c. of dry ether in a tube. No liquid compound was obtained, but, on long keeping, crystals formed in the tube.

Mixed Halogen Salts and Ether.

Lithium Bromide, Mercuric Iodide, and Ether.—0·45 Gram of lithium bromide and 2·27 grams of mercuric iodide were mixed with 3 c.c. of dry ether in a sealed tube. The salts liquefied, taking up 2·15 c.c. of ether. From these numbers the formula $LiBr,HgI_2,4Et_2O$ is derived.

Lithium Iodide, Mercuric Bromide, and Ether.—0·76 Gram of lithium iodide and 2·15 grams of mercuric bromide liquefied in contact with 4 c.c. of dry ether, and required 3·14 c.c. for solution; hence the formula of the compound is $LiI,HgBr_2,5Et_2O$. Neither lithium chloride with mercuric iodide nor lithium iodide with mercuric chloride gave any liquid compound with ether.

Lithium Bromide, Mercuric Chloride, and Ether.—0·85 Gram of lithium bromide and 2·65 grams of mercuric chloride were mixed with 4 c.c. of dry ether. The action was slow and did not appear complete, but partial liquefaction occurred. The amount of ether taken up was 1·06 c.c.; hence the probable formula of the compound is $LiBr,HgCl_2,Et_2O$.

Lithium Chloride, Mercuric Bromide, and Ether.—0·21 Gram of lithium chloride and 1·8 grams of mercuric bromide became pasty in contact with 2 c.c. of dry ether without completely liquefying. The amount of ether taken up was 0·7 c.c.; hence the probable formula of the compound is $LiCl,HgBr_2,Et_2O$.

All the liquid compounds with ether mentioned above contain a mercury salt as one constituent. The following are examples of liquid ether compounds, where silver, lead, and copper iodides take the place of mercury salts.

Lithium Iodide, Silver Iodide, and Ether.—1·82 Grams of lithium iodide and 2·67 grams of silver iodide were sealed with 6 c.c. of dry ether in a tube. Liquefaction took place rapidly, two layers were formed, and 3·6 c.c. of ether were taken up. From this the formula $LiI,AgI,3Et_2O$ is deduced.

Lithium Iodide, Copper Iodide, and Ether.—1·45 Grams of lithium iodide and 2·05 grams of cuprous iodide were sealed in a tube with 5 c.c. of dry ether. A liquid compound was obtained, but was not clear. The ether not used was 0·85 c.c. Hence the probable formula of the compound is $LiI,CuI,4Et_2O$.

Lithium Iodide, Lead Iodide, and Ether.—0·87 Gram of lithium iodide and 2·62 grams of lead iodide were sealed in a tube with 4 c.c. of dry ether. Ether was absorbed, and the compound formed was solid and crystalline. It melted partly on warming, but a clear liquid was not formed. The composition is doubtful; apparently between 3 and 4 molecules of ether are required.

UNIVERSITY MUSEUM,
OXFORD.

CCXLII.—*The Relation between the Crystal Structure and the Chemical Composition, Constitution, and Configuration of Organic Substances.*

By WILLIAM BARLOW and WILLIAM JACKSON POPE.

DURING the last few years the authors have investigated a novel method of studying the relations between crystalline and molecular structure, and have demonstrated the existence of a very simple relation between the two species of structure in a great variety of cases (Trans., 1906, **89**, 1675; 1907, **91**, 1150; 1908, **93**, 1528); the principles involved in the method referred to were briefly summarised in the introduction of the last-mentioned communication. One of the chief results of this work has been to demonstrate that, in a given crystalline substance, the volumes appropriated by the spheres of influence of the different atoms contained in the molecule are approximately proportional to the numbers representing the respective fundamental valencies; this conclusion has been independently verified for hydrocarbons and their simple derivatives containing oxygen or nitrogen in the liquid state by Le Bas (Trans., 1907, **91**, 112; *Phil. Mag.*, 1907, [vi], **14**, 324; 1908, **16**, 60). The latter author, indeed, carries the valency law a step further by showing that throughout a series of liquid hydrocarbons, under corresponding conditions, the atomic volumes are directly proportional to the numbers representing the fundamental valencies of the elements carbon and hydrogen.

In view of the close relation which has been shown to exist between the sum of the fundamental valencies of the atoms composing the molecule—the valency volume—and the crystalline structure affected by the substance, it is convenient to derive constants for related series of substances which are simple functions of the valency volume and of the crystalline structure as expressed by the geometrical data. We have therefore introduced the so-called "equivalence parameters," x, y, and z, which are the lengths of the edges of a parallelepidon, of which the volume is the valency volume, W, and of which the relative linear and angular dimensions accord with the axial ratios and the interaxial angles (Trans., 1906, **89**, 1681); the equivalence parameters are calculated as follows:

$$x = \sqrt[3]{\frac{a^2 W}{c \sin A \sin \beta \sin \gamma}},\ y = x/a \text{ and } z = cy.$$

The important nature of the information to be obtained by the aid of the equivalence parameters has been fully demonstrated in our previous papers, and by Jaeger (Trans., 1908, **93**, 517), Jerusalem (Trans., 1909, **95**, 1275), and Armstrong (this vol., p. 1578).

In the present paper we propose to discuss the close-packed assemblages representing the molecular composition, constitution, and configuration of the paraffinoid, ethylenic, and acetylenic hydrocarbons. As a result of this investigation we shall be able to show that, adopting the same principles as have been previously laid down, each hydrocarbon has its own specific kind of structural unit, and that geometrical peculiarities are distinguishable in the appropriate assemblages corresponding with the presence in the molecule of single, double, and triple bonds between carbon atoms. It will further be shown that the configurations derived for the various hydrocarbons by closely packing spheres of magnitudes appropriate for representing the spheres of influence of their atoms are in accordance with the conclusions of van't Hoff and Le Bel concerning the environment of a methane carbon atom. Finally, it will be shown that a process of simple adjustment furnishes a geometrical interpretation of polymerisation and isomeric change, such, for instance, as the conversion of acetylene into benzene. As a preliminary to the main argument, and in justification of the methods employed, a passing reference may be made to one or two simple considerations and the data supporting them.

Concerning the legitimacy of attributing to carbon a sphere of atomic influence four times as large as that of hydrogen, little more now remains to be said. Since we first drew this conclusion, Le Bas has conclusively proved the atomic volume of carbon to be four times that of hydrogen, and Jerusalem has shown the same relation to hold approximately as between crystalline substances which are not examined under strictly corresponding conditions. Most of the hydrocarbons of the series with which we have now to deal are, however, either liquid or gaseous under ordinary conditions, and therefore yield no crystallographic data for employment as a direct experimental check. For our present purpose it is consequently necessary to use crystallographic data referring to the halogen derivatives of hydrocarbons, and to rely on them to furnish the necessary check on the dimensions of the hydrocarbon assemblages described. The legitimacy of the use of these derivatives for this purpose depends on our previous conclusion that the spheres of atomic influence of hydrogen and the halogens differ but slightly in volume when contained in the same molecular complex (Trans., 1906, **89**, 1679), although the sphere of atomic influence of hydrogen is somewhat smaller than those of the halogens (Trans., 1907, **91**, 1197). That the spheres of atomic influence of hydrogen and the halogens have approximately the same valency volume may be conveniently demonstrated by showing that the chemical substitution of a halogen atom for one of hydrogen in a crystalline substance is frequently not accompanied by a profound change in axial dimensions; in the instances quoted below, it will be seen that the geometrical change accompanying the substitution in question is in general greater than that ordinarily observed in cases of isomorphism, but not so great as to obscure the obvious morphotropic relationship. The comparatively large change in axial dimensions which is in general thus presented, and also the rarity of such instances, must be attributed to the sphere of atomic influence of hydrogen differing appreciably in magnitude from those of chlorine, bromine, or iodine, the latter being much more nearly of the same size; the discrepancy in volume between the spheres of hydrogen and of the halogens is, however, not sufficient to necessitate the employment of different sizes of spheres of influence for those elements in the construction of the close-packed assemblages described below.

The substitution of hydrogen by bromine, unaccompanied by considerable changes in axial dimensions, is illustrated by the data for the monosymmetric pentabromoethane and the orthorhombic hexabromoethane (Trans., 1906, **89**, 1682):

$CHBr_2{\cdot}CBr_3$	$a : b : c = 0{\cdot}5650 : 1 : 0{\cdot}3118$; $\beta = 91°19'$
$CBr_3{\cdot}CBr_3$	$a : b : c = 0{\cdot}5639 : 1 : 0{\cdot}3142$; $\beta = 90°$

A similar case is presented by the orthorhombic π-sulphonyl chlorides and bromides of camphor and of α-bromo- and α-chlorocamphor (Kipping and Pope, Trans., 1893, **63**, 548; 1895, **67**, 367):

d-$C_{10}H_{15}O{\cdot}SO_2Cl$	$a : b : c = 0{\cdot}9950 : 1 : 1{\cdot}0368$
d-$C_{10}H_{15}O{\cdot}SO_2Br$	$a : b : c = 0{\cdot}9816 : 1 : 1{\cdot}0249$
d-$C_{10}H_{14}OBr{\cdot}SO_2Cl$	$a : b : c = 0{\cdot}8912 : 1 : 1{\cdot}0518$
d-$C_{10}H_{14}OCl{\cdot}SO_2Br$	$a : b : c = 0{\cdot}8795 : 1 : 1{\cdot}0494$

The axial dimensions of the monosymmetric *p*-azoxytoluene and its monobromo-derivative are almost identical (v. Zepharovitch, *Zeitsch. Kryst. Min.*, 1889, **15**, 214), and a similar relationship holds between the values for the orthorhombic *p*-tolyl-mono- and di-chloro-methylsulphones (Brugnatelli, *Zeitsch. Kryst. Min.*, 1892, **20**, 604—605):

p-Azoxytoluene	$a : b : c = 1{\cdot}4971 : 1 : 1{\cdot}0196$; $\beta = 75°30'$
Bromo-*p*-azoxytoluene	$a : b : c = 1{\cdot}5194 : 1 : 1{\cdot}01$; $\beta = 75°28'30''$
p-Tolylmonochloromethylsulphone	$a : b : c = 0{\cdot}6070 : 1 : 0{\cdot}7865$
p-Tolyldichloromethylsulphone	$a : b : c = 0{\cdot}5324 : 1 : 0{\cdot}7912$

Acetamide is rhombohedral with $a : c = 1 : 0{\cdot}5916$ (Kahrs, *Zeitsch. Kryst. Min.*, 1905, **40**, 476); on referring the substance to rectangular axes by changing the indices {100}, {101}, and {110} to {110}, {301}, and {301} respectively, the values are obtained as:

$$a : b : c = 1{\cdot}6904 : 1 : 0{\cdot}9759 ;\ \beta = 90°.$$

Dibromoacetamide is monosymmetric with $a : b : c = 1{\cdot}6887 : 1 : 1{\cdot}2785$, $\beta = 87°2'$ (Fock, *Zeitsch. Kryst. Min.*, 1888, **14**, 538); when the transposition involved in changing the indices of {203} to {101} is made, the axial ratios are obtained as $a : b : c = 1{\cdot}6887 : 1 : 0{\cdot}8625$, $\beta = 87°2'$. The change of indices here made is legitimate, because the form {203} is actually observed. Tribromo- and trichloro-acetamide are also monosymmetric, and exhibit the axial ratios $a : b : c = 1{\cdot}7339 : 1 : 0{\cdot}8636$, $\beta = 79°37'$, and $1{\cdot}7485 : 1 : 0{\cdot}8490$, $\beta = 78°36'$ respectively. The four sets of axial ratios show a fairly close agreement.

The orthorhombic monochloro-*p*-benzoquinone exhibits the axial ratios, $a : b : c = 1{\cdot}7461 : 1 : 0{\cdot}9619$ (Fels, *Zeitsch. Kryst. Min.*, 1903, **37**, 479); these ratios, expressed in the form $b : c : a =$

1·0396 : 1 : 1·8153, closely approximate to those of the monosymmetric dichloro-*p*-benzoquinone (Fock, *Zeitsch. Kryst. Min.*, 1883, **7**, 40), namely, $a : b : c = 1·0920 : 1 : 1·8354$, $\beta = 89°11'$, and dibromo-*p*-benzoquinone (Fels, *loc. cit.*), which exhibits $a : b : c = 1·0941 : 1 : 1·8229$, $\beta = 92°32'$. The three substances are, however, pseudohexagonal, and the morphotropic relation between them is probably even closer than is indicated by the above axial ratios. Thus, on changing the forms $\{10\bar{1}\}$, $\{101\}$, $\{100\}$, and $\{103\}$ observed on dibromo-*p*-benzoquinone to $\{001\}$, $\{101\}$, $\{103\}$, and $\{100\}$ respectively, the axial ratios become $a : b : c = 1·7416 : 1 : 0·9491$, $\beta = 90°41'$. These values approximate much more closely to the original ones given above for monochloro-*p*-benzoquinone than do those stated by Fels. It is in any case clear that, contrary to the views of Grünling (*Zeitsch. Kryst. Min.*, 1883, **7**, 582) and of Fels, very little change in axial dimensions attends the passage from monochloro-*p*-benzoquinone to dichloro- or dibromo-*p*-benzoquinone.

In the instances quoted above, the replacement of hydrogen by a halogen atom leads to no very profound change in crystallographic dimensions. The same kind of relation as is thus expressed must be looked for amongst halogen derivatives which are position isomerides, and several instances from amongst such substances may next be quoted.

The di- and tri-halogen derivatives of camphor have been very completely examined by (1) v. Zepharovitch (*Zeitsch. Kryst. Min.*, 1883, **7**, 588), (2) Cazeneuve and Morel (*ibid.*, 1888, **14**, 267), (3) Kipping and Pope (Trans., 1895, **67**, 371), and (4) Armstrong and Lowry (*ibid.*, 1898, **73**, 579). The close morphotropic relationship between these orthorhombic substances becomes evident on interchanging the dimensions *b* and *c* in the data (1) and (2), dividing dimension *b* by two and writing *b* for *a*, *c* for *b*, and *a* for *c* in the data (3), and leaving data (4) as stated by Armstrong and Lowry; the following values are thus obtained:

		Original.	Transposed.
		$a : b : c$.	$a : b : c$.
(1)	*aa*-Dibromocamphor …………	0·7925 : 1 : 0·5143	1·5409 : 1 : 1·9943
(2)	*aa*-Dichlorocamphor …………	0·8074 : 1 : 0·5448	1·4830 : 1 : 1·8365
	aa-Bromochlorocamphor ……	0·8040 : 1 : 0·5228	1·5379 : 1 : 1·8355
(3)	*aπ*-Dichlorocamphor …………	0·6933 : 1 : 0·3297	1·5160 : 1 : 2·1029
	aπ-Dibromocamphor …………	0·6860 : 1 : 0·3323	1·5148 : 1 : 2·0856
	aπ-Chlorobromocamphor ……	0·6884 : 1 : 0·3301	1·5074 : 1 : 2·0642
	aπ-Bromochlorocamphor ……	0·6861 : 1 : 0·3317	1·5045 : 1 : 2·0684
(4)	*aa*-Chlorobromocamphor ……	1·5338 : 1 : 1·9020	1·5338 : 1 : 1·9020
	βaa-Dibromochlorocamphor …	1·4627 : 1 : 2·1332	1·4627 : 1 : 2·1332

Jaeger has shown (*Zeitsch. Kryst. Min.*, 1904, **38**, 570) that the monosymmetric position isomerides, the 1 : 2 : 4- and the 1 : 3 : 4-tri-bromotoluenes, have almost identical axial ratios, namely, $a:b:c=3{\cdot}5283:1:4{\cdot}1958$, $\beta=58^\circ47'$, and $a:b:c=3{\cdot}5470:1:4{\cdot}2603$, $\beta=58^\circ55'$, respectively.

A large number of instances similar to those quoted above might be selected from the crystallographic literature, but the above will suffice to confirm our previous conclusion that the sphere of atomic influence of hydrogen differs but slightly in volume from those of the halogen elements, and consequently that they are all represented in the close-packed, homogeneous assemblage with sufficient exactness by spheres of the same size. In the following pages we shall therefore assume that the crystallographic configuration of any hydrocarbon can be presented under some conditions by its halogen derivatives, and, when crystallographic data are available for any of the latter, shall directly employ those data for checking the correctness of the assemblage derived for the hydrocarbon itself. In connexion with the concluding portions of this communication, in which the occurrence of polymerisation and isomeric change is treated, it may possibly be suggested that no method of discussion involving considerations connected with crystal structure can be justified, inasmuch as such changes occur in general in the liquid or even in the gaseous state. To this objection the reply is made that the great mass of work done during recent years on so-called liquid crystals has greatly extended the domain of crystal structure. It is now known that in those liquid substances which exist in the liquid crystalline condition, tracts, so large as to be readily discerned microscopically, exist in which the regularity of arrangement exhibited by solid, crystalline structures is present. These tracts are continually forming and disappearing, and their occurrence indicates clearly that in these mobile liquids the particles aggregate themselves together in masses which, measured on a molecular scale, are of enormous extent, and in which very complete regularity of structure prevails. Since, in such instances as these, the eye can discern the existence of a liquid, crystalline structure, it is legitimate to assume that in liquids generally, arrangements of parts, comparable in regularity with crystalline structures, are being continually formed and dissolved, although possibly not to such an extent as in the cases of known liquid crystals. The occasional juxtaposition of parts in orderly close-packed arrangement thus premised is all that is required to legitimise the discussion of isomeric change in connexion with crystalline structure.

Methane.

As a preliminary to an attempt to apply the methods which we have previously described to the elucidation of the configurations and properties of the paraffins, it is necessary briefly to enumerate the available chemical and crystallographic facts and conclusions bearing on the configuration of the simplest paraffin, methane. The following may be quoted as sufficient to lead to the construction of the homogeneous close-packed assemblage of spheres which represents this hydrocarbon.

(1) In accordance with the conclusions respecting valency which we have previously drawn (Trans., 1906, **89**, 1723), the space appropriated in the methane assemblage by each carbon atom should be four times as large as that appropriated by each hydrogen atom.

(2) Carbon tetrabromide, CBr_4, possesses the same configuration as methane, and its assemblage will be represented by the same spheres. The halogen derivative is dimorphous, crystallising above 47° in the cubic system (Rothmund, *Zeitsch. physikal. Chem.*, 1897, **24**, 712) and at the ordinary temperature in the monosymmetric system. Carbon tetrachloride and tetraiodide crystallise in the cubic system.

(3) Stereochemical facts indicate that in the free methane molecule the four hydrogen atoms are situated at the apices of a regular tetrahedron described about the carbon atom, and that this tetrahedral environment of the methane carbon atom must be regarded as surviving a substitution of one or more of the four hydrogen atoms by other atoms or radicles.

(4) The assemblage representing methane, built up in accordance with the principles laid down in previous papers, should be capable of geometrical modification so as to yield assemblages representing other paraffins; the geometrical process thus involved should be strictly illustrative of the practical methods by which methane can be converted into these homologous paraffins. It should thus be possible to derive one assemblage corresponding in composition, constitution, and configuration with each paraffinoid hydrocarbon. An extension of the same method should lead to the derivation of characteristic assemblages for other aliphatic hydrocarbons and compounds other than the paraffins; the applications should embrace all the varieties of isomerism, and express the facts that have led to the conception of the asymmetric carbon atom.

An assemblage which, both as a whole and when partitioned, fulfils the above and other conditions concerning methane is arrived at in the following manner. Alternate layers are removed from a cubic closest-packed assemblage of equal incompressible but deformable spheres (Trans., 1907, **91**, 1152), regarded as composed of layers of square arrangement (Fig. 1), the remaining layers being caused to retain their original positions. The resulting skeleton assemblage, which has tetragonal symmetry, is shown in plan and elevation in Figs. 2 and 3; the dotted lines which join the centres of nearest spheres in the three principal directions outline a partitioning of space into equal right square prisms.

The next step consists in distorting the skeleton assemblage by a contraction along its fourfold axis, accompanied by a compensatory expansion in directions transverse to this axis, so that the sphere centres finally lie at the corners of cubes equal in content or volume to the original right square prisms. The system thus derived possesses holohedral cubic symmetry, and is composed of spheres which do not quite touch one another; its projection parallel to any cube plane is shown in Fig. 4. This cubic system, like the tetragonal system from which it is derived, possesses one-half the density of packing of the parent assemblage; if, therefore, small spheres of the same deformable material, four times as numerous and one-fourth the volume of the original large ones, are forced into its cavities, and the whole system is then subjected to compression so as to eliminate the interstitial space, the polyhedra produced from the large spheres will be about four times as large as

FIG. 1.

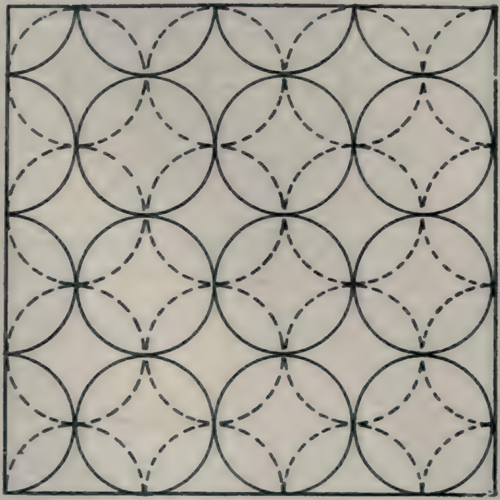
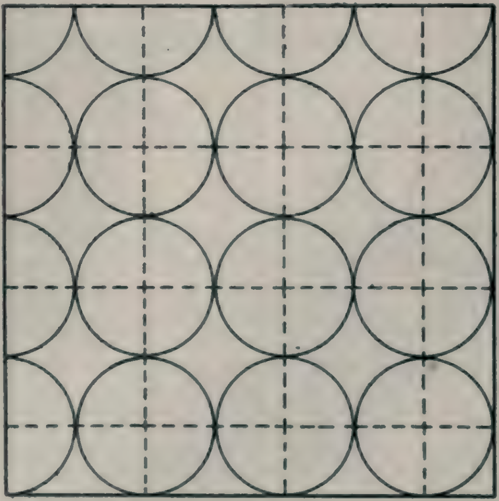


FIG. 2.



those produced from the small ones. In the skeleton assemblage of Fig. 4, the cavities are as numerous as the spheres; if, therefore, each cavity bounded by eight neighbouring spheres can be made to accommodate a group of four of the small spheres in such a manner as to give stable equilibrium and to be compatible with cubic symmetry, several of the more essential conditions for methane will be obeyed by the assemblage.

FIG. 3.

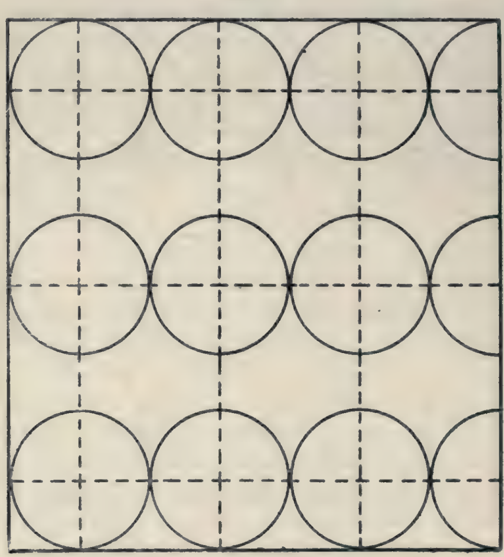
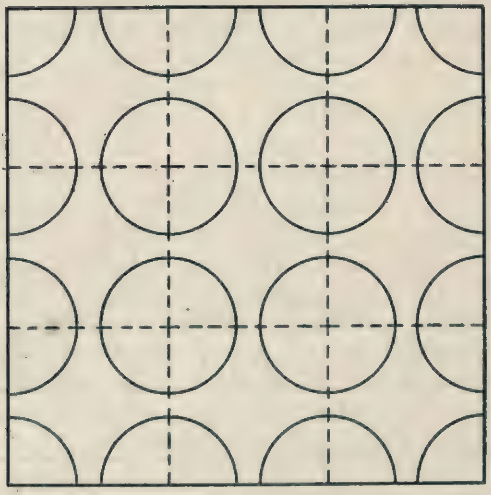


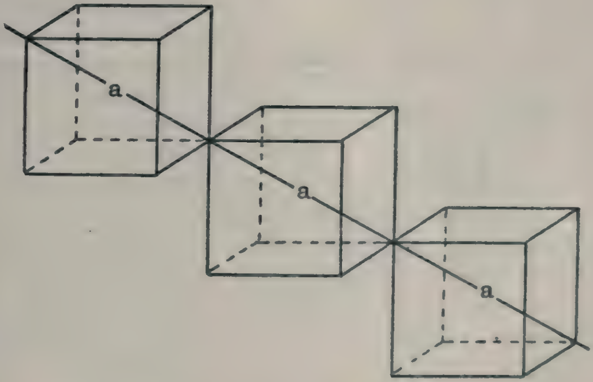
FIG. 4.



Each cavity of the skeleton assemblage described exhibits six identical four-sided hollows, the centres of which lie on three rectangular axes drawn through the centre of the cavity, and, in placing a tetrahedral group of the small spheres within the latter, any three of the hollows which lie nearest together are selected for the reception of three out of the four small spheres of the group, one jutting into each of the selected hollows. The fourth sphere of the tetrahedral group will then touch that sphere of the eight of volume four which does not border either of the selected hollows, the point of contact being on the cube diagonal which passes through the centre of this large sphere. The marshalling thus arrived at for a cubic unit of the assemblage is the one required; it has yet to be shown what relative orientations of the contents of the different cube cells are consistent with cubic symmetry and what adjustment of the arrangement described will restore the close-packing which has been impaired by substituting the tetrahedral groups of small spheres for one-half of the larger spheres of the closest-packed assemblage.

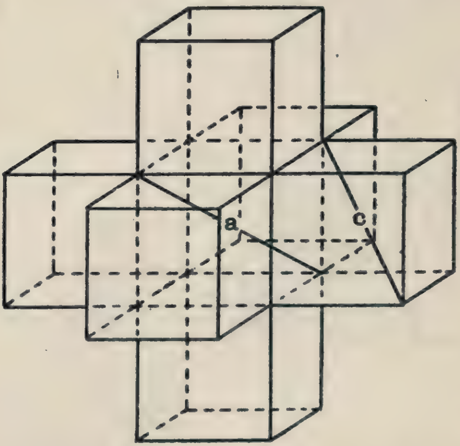
The introduction of the tetrahedral group into the cubic cell in the manner described lowers the symmetry by destroying three of the four trigonal axes of the cell; if cubic symmetry is to survive the introduction of such a tetrahedral group into each cavity, the arrangement of the completed assemblage must consequently be of one of the types in which the trigonal axes do not intersect. The mode of ascertaining the relative positions of the non-intersecting trigonal axes has been already described (Trans., 1907, **91**, 1183); its application to the present case leads, in the following manner, to the production of the appropriate type of symmetry for the methane assemblage.

FIG. 5.



In the cubic partitioning of space shown in Fig. 4, one trigonal axis, *a*, of one cube of the partitioning is drawn and produced in both directions, so as to pass through a string of cubic cells which are in contact at their corners (Fig. 5), the latter being centres of carbon spheres; in the first selected cube of the partitioning, the group of four small or hydrogen spheres is inserted in its appropriate position with respect to this trigonal axis. In any one of the six cubic cells which make face contact with the first selected cube cell, a single diagonal is drawn, the position chosen being such that, like *c* in Fig. 6, it is not parallel to the trigonal axis *a*, already located and does not intersect it. This last drawn diagonal is used as a trigonal axis, and by rotations about it through 120°, the existing trigonal axis and group of small spheres are transferred to two new positions, so as to locate other trigonal axes and groups of hydrogen spheres in the system. The latter process is repeated about the axes thus located and about subsequently located axes, until all the situations for trigonal axes in their four orientations and all the positions for groups of small spheres derivable in this manner have been ascertained; the minimum distance separating trigonal axes of different orientations is that separating the two first located. A diagram showing the relative situations of the axes has been already given (Trans., 1907, **91**, 1183).

Fig. 6.



As a result of this series of operations, one trigonal axis becomes located in each cube cell of the cubic partitioning of space, but the original tetrahedral group of small spheres becomes transferred to but one-half of these cube cells. The cube cells forming the half system, distinguished by each cell containing a tetrahedral group of small spheres, are in contact at their edges only; they have the arrangement of the light or the dark cubes of the previously described stack of cubes of two kinds (Trans., 1908, **93**, 1533, Fig. 1). The skeleton assemblage thus derived has the symmetry of Barlow's type 1.

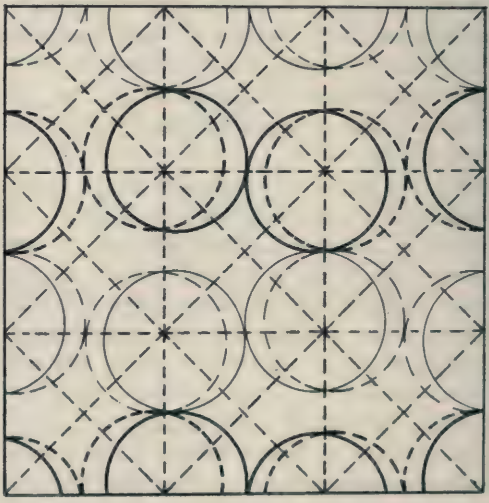
Only one kind of arrangement possessing cubic symmetry can be arrived at in the manner just described, but there are two alternative ways in which to complete the assemblage homogeneously by filling the unoccupied cavities, which are equal in number to those occupied, with the tetrahedral groups of small spheres in a manner compatible with cubic symmetry; both of these involve slight adjustment of the skeleton assemblage, but no re-marshalling. The completion is in both cases effected by bringing the one-half system of cubes to the place of the other half system. One of the two alternative operations consists in rotating the system through 180°

about an axis drawn perpendicular to a cube face and passing through the centre of a cube edge, such perpendicular not being a digonal screw axis of the skeleton assemblage; this involves the addition of digonal rotation axes to the original system of trigonal axes and digonal screw axes, and yields a completed assemblage having the symmetry of Barlow's type 2. The other operation is one performed about a centre of symmetry situated at a cube angle, and leads to the production of a completed assemblage having the symmetry of Barlow's type 1*a* (*Zeitsch. Kryst. Min.*, 1894, **23**, 10, 44). Both assemblages thus derived become very closely packed as the result of a slight adjustment, but the assemblage of type 2, which displays tetartohedral cubic symmetry, appears to be capable by modification of closer packing than the other. It is, moreover, the assemblage indicated by the facts as representing methane; each of the large spheres in it is similarly situated with respect to the groups of small spheres, whilst in the assemblage of type 1*a* the large spheres form two sets, the members of one of which differ in environment from those of the other. The latter type of assemblage probably has a practical application, although not in the present connexion.

With respect to the relative orientation of the tetrahedral groups of small spheres in the assemblage of type 2, it is to be noted that the groups contained within the one half set of the cubes of the partitioning are related by a simple operation, besides that of rotation about a digonal axis, to those contained within the other half set. The relation consists in the existence of four similar translations having the four directions of the sets of trigonal axes. Either of these operates to bring a cubic cell to the place of a neighbouring cubic cell, which is in contact with the first at one of its corners. In addition to being identical, the two half systems of cubes with their contained groups of four small spheres consequently have the same orientation, and the assemblage as a whole is hemimorphous, like the assemblage of type 1 from which it is derived.

It has been already noticed that in order to render the packing close, a modification or deformation of the whole assemblage must occur. The eight large or carbon spheres enclosing a single cavity may be regarded as forming six indivisible quartettes, one for each of the six faces of the cubic cell containing the cavity; the four spheres composing a quartette form two square hollows, one in each of its opposite faces, and these two hollows communicate with each other at the centre of the quartette. Where a small sphere occupies the hollow on one face, the existence of a digonal axis bisecting the cell face involves the presence of another small sphere in the hollow on the other face of the same quartette, and therefore one half of the quartettes of large spheres in the assemblage are occupied, and the other half unoccupied, by the smaller spheres. It follows that some increase in the closeness of the packing will be likely to supervene if it is possible symmetrically to adjust the arrangement of the larger spheres, without altering the marshalling, in such a way as similarly to diminish the size of one-half of the hollows—the unoccupied ones—while slightly increasing the size of the rest—the occupied ones. Three of the six hollows present in each cavity, namely, the unoccupied ones, will in this event become contracted. Such an adjustment of the larger spheres, which does not alter the type of symmetry, consists in a slight equal shift of each large sphere along its trigonal axis in either direction; the choice made of the direction of shift for any one sphere necessarily determines the directions for all if the assemblage is to remain compatible with the coincidence movements of type 2. The amount of shift is limited by the approximation of the large spheres, causing them to come into contact at points lying on the digonal axes of rotation which characterise type 2. An important feature of the change is that the large or carbon spheres, in shifting, close in around that hydrogen sphere of each tetrahedral group the centre of which lies on the trigonal axis; the position of the tetrahedral groups undergoes slight adjustment during the process.

FIG. 7.



A projection of the resulting assemblage, showing the carbon spheres alone, is given in Fig. 7; the centres of these spheres lie in four different planes parallel to the plane of projection, and are therefore distinguished by circles drawn in heavy or light, continuous or broken lines. The adjustment of the positions of the tetrahedral groups which accompanies the shifting of the carbon spheres, and indeed the entire process, is compatible with the maintenance of cubic symmetry; the existence of the coincidence movements of the system involves that all the cavities for the reception of the tetrahedral groups remain identical with one another.

One of the surest indications of close-packing is obtained when each sphere is in contact with, or in very close proximity to, such a number of surrounding spheres as approaches the maximum. The number of contacts and near proximities in the assemblage under consideration is as follows: for each of the carbon spheres, 19, namely, 6 with carbon spheres and 13 with hydrogen spheres. For each of three-fourths of the hydrogen spheres, 8, namely, 4 with carbon spheres and 4 with hydrogen spheres; for each of one-fourth of the hydrogen spheres, 7, namely, 4 with carbon spheres and 3 with hydrogen spheres. These numbers of contacts approach the maxima, taking into account the different sizes of the component spheres; they thus afford a proof that the marshalling of the assemblage is compatible with very close-packing.

In connexion with the partitioning of the assemblage into identical molecular units of the composition CH_4, it should be noted that four of the thirteen contacts of hydrogen spheres with a carbon sphere are nearly symmetrically distributed over the surface of the latter; the four hydrogen spheres concerned are thus situated at the apices of an approximately regular tetrahedron, of which the centre is the centre of the carbon sphere. The four hydrogen spheres referred to may be identified as follows. In any pseudo-cubic group of eight carbon spheres in the assemblage, the single trigonal axis intersects two of the eight; one of these makes contact with a single hydrogen sphere of the enclosed group at its point of intersection with the trigonal axis. Regarding this carbon sphere as that of the molecular unit, CH_4, to be picked out, it is to be noted that the three contacts with it of hydrogen spheres, which, with the one on the trigonal axis, make up the four referred to, are those of the hydrogen spheres lying in three of the outside hollows of those faces of the cubic group which have as their common angular point the centre of the selected carbon sphere. The four contacts of the unit molecular group CH_4 thus derived do not precisely mark the angular points of a regular tetrahedron, but the arrangement of the four hydrogen spheres about the carbon sphere approximates so closely to the regular tetrahedral disposition premised by the theory of van't Hoff and Le Bel (Figs. 8 and 9) that its departure from the latter cannot be clearly indicated in a diagram; the assemblage is divisible into identical units of the form depicted. The result of the close approximation to regularity of the tetrahedra marked out by the hydrogen sphere centres thus selected is that different assemblages produced by fitting together the molecular units in different orientations will be so nearly identical that the equilibrium arrangements to which they pass will be actually identical. In this connexion it is instructive to observe that the tetrahedral arrangement is indicated in another manner; each carbon sphere, before the adjustment, is similarly related to eight cavities, of which the relative positions are those of the angular points of a cube, and the greatest number of these cavities which can participate in containing the hydrogen spheres attached to the carbon sphere is four. Consequently, the most symmetrical mode of allotment of the hydrogen spheres is for each carbon sphere to attach to itself four hydrogen spheres contained in four out of the eight cavities surrounding it, and for these four cavities to be selected with a regular tetrahedral disposition. Thus, like the hydrogen atoms in the usual graphic formula of methane, the four cavities concerned have interchangeable positions with respect to the carbon sphere to which they relate.

FIG. 8.

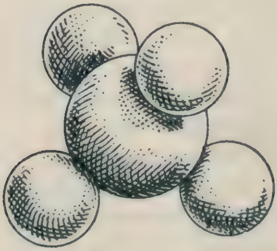
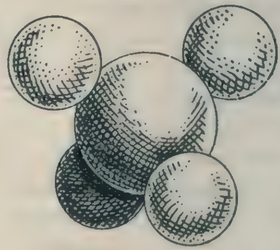


FIG. 9.



It is thus to be finally concluded that the investigation of the close-packed arrangement of the methane assemblage indicates that the molecular units can be so chosen as to have the tetrahedral configuration depicted in Figs. 8 and 9.

The relation thus established between the theory of the tetrahedral arrangement of the links within the molecule, based on the chemical behaviour of methane and its derivatives, and the concrete geometrical properties of the corresponding close-packed arrangement of the spheres of influence of the component atoms is of fundamental importance. It is worth recapitulating in precise language, because it will subsequently be shown that a relation of the same nature obtains for the carbon compounds generally; in other words, that a tetrahedral arrangement of the contacts of a carbon sphere of influence with its companion spheres persists after substitution has taken place. The relation for methane may be thus stated. Represent the carbon and hydrogen atoms of a methane molecule by spheres of the valency volumes 4 and 1 respectively, and form the spheres into groups of five according to the van't Hoff-Le Bel theory, each sphere of volume 4 being in contact with four spheres, each of volume 1, placed around it symmetrically, so that their centres mark the angular points of a regular tetrahedron; it is then found that, while preserving the marshalling of the spheres of each individual molecular unit, a close-packed assemblage can be formed by fitting the groups together symmetrically, of such a nature that its geometrical properties are those of the crystalline tetrahalogen derivatives of methane.

The following crystallographic data are available as bearing on the symmetry and dimensions of the methane assemblage. Carbon tetraiodide, CI_4, is cubic, and carbon tetrabromide, CBr_4, crystallises above 46·7° in the cubic system, the crystal class being known in neither case. Below 46·7°, carbon tetrabromide crystallises in the monosymmetric system, but, as previously pointed out (Trans., 1908, **93**, 1530), this modification is referable to the pseudocubic axial system, $a:b:c=1·0260:1:1$, $\alpha=90°16'$, $\beta=\gamma=90°33'$; the monosymmetric form thus scarcely differs in dimensions from the truly cubic one, and both indicate the cubic marshalling of the assemblage. On replacing each hydrogen sphere in the methane assemblage by the group CH_2Br, in accordance with the second geometrical property of close-packed assemblages (Trans., 1907, **91**, 1204), tetrabromo-ββ-dimethylpropane, $C(CH_2Br)_4$, is obtained; as Jaeger has found (Trans., 1908, **93**, 520), this substance may be regarded as pseudocubic, with the axial ratios $a:b:c=1·0484:1:0·9472$, $\beta=90°45'$. The cubic marshalling of the methane or carbon tetrabromide assemblage thus survives the symmetrical introduction of four methylene groups, CH_2, into each molecular unit, CBr_4, in accordance with the second geometrical property.

In connexion with the assemblage attributed above to methane and to its fully substituted halogen derivatives, it may be noted that iodoform, CHI_3, is described as hexagonal with $a:c=1:1·1084$ (Pope, Trans., 1899, **75**, 46). It is evident that the symmetry of the space arrangement of the methane assemblage may be lowered without any appreciable alteration of the relative situations of the spheres by a partial substitution of the spheres representing hydrogen atoms which leads to the production of an arrangement appropriate for iodoform. In order to trace the probable effect of such a substitution, it is convenient to work with an ideal less closely-packed assemblage of higher symmetry, from which the methane assemblage may be regarded as derived. Let the centres of the carbon spheres occupy precisely the points of a cubic space-lattice (Fig. 3), and let each of the tetrahedral groups, CH_4, which are now to be of completely regular configuration, be rotated from the orientations which they present in the closest-packed assemblage, so that the centres of the small spheres all lie on trigonal axes; the system thus consists of units of the composition CH_4, less closely packed, but all similarly orientated. Next substitute iodine spheres for three of the four hydrogen spheres of each unit, without altering the positions of the centres, in such a way that the new units, CHI_3, are all similarly orientated; the result is to destroy three-fourth of the trigonal axes, and to leave only those which contain the centres of the unsubstituted hydrogen spheres. On performing finally the rotations and adjustments requisite to restore the closest-packed condition prevailing in the methane assemblage, three-fourths of the surviving trigonal axes are destroyed. The closest-packed assemblage thus arrived at has rhombohedral symmetry and is pseudocubic.

In the assemblage just derived let the dimension c be three times the distance between the centres of carbon spheres lying on the same trigonal axis; the distance separating these centres along directions perpendicular both to this axis and to a face diagonal of a cube of the pseudocubic partitioning will be approximately $\sqrt{2}.c/3$. If the latter distance is taken as $a/2$, the axial ratio is obtained as:

$$a:c=2\sqrt{2}:3=1:3/2\sqrt{2}=1:1{\cdot}0606.$$

This ratio is not far removed from that of iodoform, and it is therefore established that the rhombohedral form displayed by the crystalline substance may, like the rhombohedral assemblage suggested, be pseudocubic.

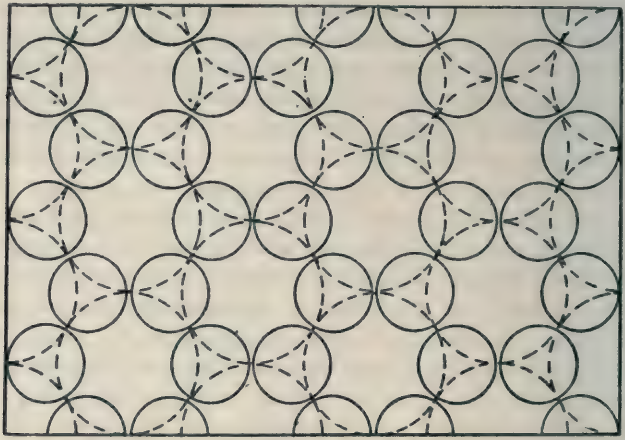
The Normal Homologues of Methane.

The most obvious method of constructing assemblages representing hydrocarbons homologous with methane consists in symmetrically removing one or more hydrogen spheres from the groups of four contained in the assemblage of the parent hydrocarbon, and then, by appropriate adjustment of the spheres remaining, to close up the gaps which have been produced.

Thus, an assemblage of the empirical composition CH_3 may be derived by symmetrically removing a hydrogen sphere from each group of four in the methane assemblage, and then adjusting so that with the same number of cavities each cavity among the carbon spheres shall be as closely packed as possible, although now containing but three hydrogen spheres instead of four. Such an operation corresponds with the removal of the iodine atom from methyl iodide; the observed fact that in this reaction, as in all similar ones, the condensation of two hydrocarbon radicles yields one molecule, finds expression in the way in which the assemblage undergoes contraction during the adjustment necessary for closing up the produced gaps. The fact that the methyl iodide assemblage, which has the same marshalling as that of methane, yields ethane on treatment with sodium, can be represented as follows: In the methane assemblage, the carbon spheres are prevented from making intimate contact with one another by the presence of hydrogen spheres packed around them, but when the number of the latter is reduced by each group of four becoming a group of three, the carbon spheres necessarily draw nearer together; it is conceivable that equilibrium, represented by close-packing, requires them to come into closer contact, and to press on each other two by two, and that the intimate relationship thus established between the individuals of a pair corresponds with the linking between the two methyl carbon atoms in the ethane molecule. It will be shown in connexion with the assemblage described below that the condensation of the assemblage following elimination of hydrogen spheres and the adjustment which restores close-packing, lead to close contact of the kind referred to between carbon spheres; such contact is thus representative of the formation of a link between carbon atoms such as that present in the ethane molecule.

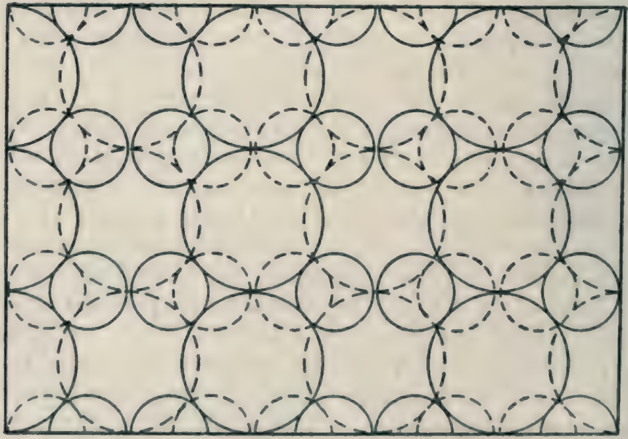
The production of the ethane assemblage from that of methane may also be regarded as resulting from the replacement of one-fourth of the hydrogen spheres, each by one carbon sphere, when, in accordance with the second geometrical property of close-packed assemblages, the introduction of three hydrogen spheres with each new carbon sphere suffices for the preservation of close-packing. The alternative ways in which the paraffins may be regarded, such, for instance, as the possibility of considering propane as dimethylmethane and as ethylmethane, also find expression in the geometrical mode of regarding these substances now advanced. The most general method of formulating the normal paraffins consists in assigning to them the constitution $H\cdot[CH_2]_n\cdot H$, in which an open chain of *n*-carbon atoms forms the backbone of the molecule, and is isolated from other similar chains in front and rear by the addition of a hydrogen atom to each of the end methylene groups. For the present purpose it will therefore be convenient to derive first an assemblage of the empirical composition CH_2, corresponding with the radicle methylene; it will then be shown how this assemblage, composed of strings of methylene groups the carbon spheres of which are in close contact throughout the length of the string, is related to that of methane, and in what manner hydrogen spheres

FIG. 10.



can be homogeneously intercalated so as to divide the methylene strings of indefinite length into definite molecular groups to represent any individual normal paraffin.

FIG. 11.



The general methylene assemblage may be constructed in the following manner. Space is divided into endless hexagonal prisms, each of which is divided into identical hexagonal cells by describing a series of parallel planes perpendicular to the prism axes at a distance apart equal to the smaller diameter of the prisms. In each prismatic cell thus obtained is inscribed a sphere; the diameter of the latter will be the smaller diameter, and also the height, of the hexagonal cell. In the system produced, each cell corner marks the centre of a cavity between adjoining spheres, and about each meeting point of cell corners a small sphere is now described of such diameter as just to touch the six surrounding large spheres. The resulting system is shown in plan in Fig. 10, and in elevation in Fig. 11, and possesses a general arrangement which may be visualised by the perspective view of a fragment shown in Fig. 12. Each small sphere of the assemblage, in addition to making contact with six large spheres, is nearly in contact with three other small spheres, and each large sphere is in contact with twelve small spheres and eight large ones. If the large spheres represent carbon, and the smaller ones hydrogen atoms, the assemblage has the empirical composition CH_2; since, however, the volume of the smaller spheres is appreciably less than one-fourth that of the larger, the valency relation of the volumes requires the smaller to increase until the volumes of small and large spheres, with the addition of the appropriate proportions of interstitial space, are in the ratio of 1 : 4. This expansion of the small spheres necessarily forces the larger spheres apart, and for this to occur in such a manner that the modified system possesses maximum closeness of packing, it must take place so as to break as few of the contacts as possible in a

FIG. 12.

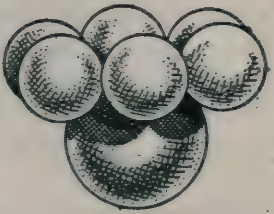
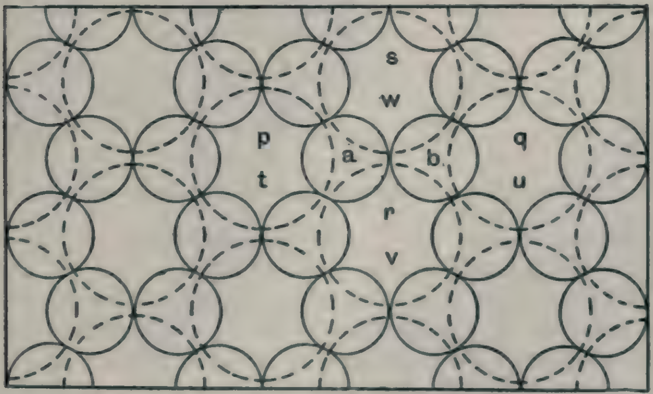


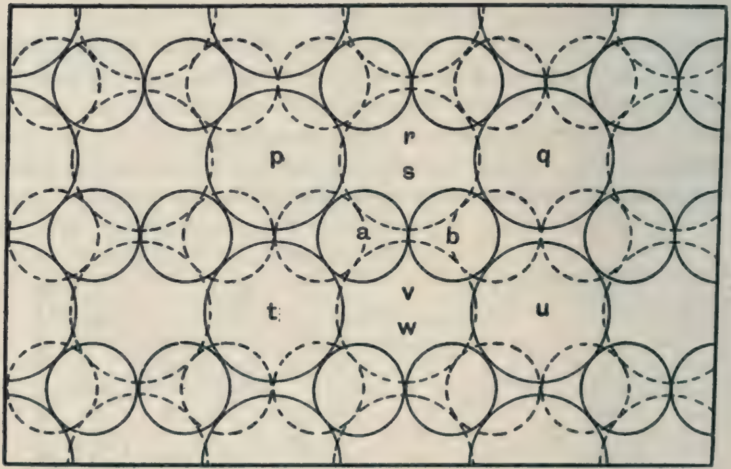
FIG. 13.



symmetrical manner. The most symmetrical expansion of the kind which can occur is one which breaks all the contacts between large spheres and converts the assemblage of Figs. 10 and 11 into that represented in Figs. 13 and 14; the smaller number of contacts in the modified system is indicative of looseness of packing, and in order to reproduce close-packing as many of the original contacts as possible must be re-established in a symmetrical manner.

A consideration of the assemblage of Figs. 13 and 14 in connexion with the cubic disposition of large spheres shown in Fig. 4, from which the methane assemblage was derived, shows that the plane arrangement of the large spheres in their layers, shown by the continuous line circles of Fig. 14, is approximately that obtaining in the layers of the assemblage of Fig. 4, which are parallel to

FIG. 14.



the plane the trace of which is the diagonal line C in Fig. 15, as shown by the continuous line circles of Fig. 16. Whilst, however, in Figs. 15 and 16 each cavity between the large spheres is destined and is sufficient for the accommodation of a tetrahedral group of four small spheres, the corresponding space in Figs. 13 and 14 has been reduced so that it can accommodate but two small spheres; this has been effected by somewhat increasing the distance between the large sphere centres in the direction of the diagonal C in Fig. 15, and considerably diminishing the distance between the layers of sphere centres in the direction perpendicular thereto. Each cavity which suffices to contain four small spheres, such as is enclosed by the eight spheres, four, p, q, r, and s, of one plane of Fig. 15, and four, t, u, v, and w, of the plane immediately below, as shown in Figs. 15 and 16, has by the process just described been converted into two cavities, namely, one enclosed by the corresponding spheres, p, r, s, t, v, and w, of Figs. 13 and 14, the other by the spheres, q, r, s, u, v, and w. The two small cavities thus derived from the original large one each suffices for the accommodation of one small sphere; these are marked a and b in Figs. 13 and 14.

Fig. 15.

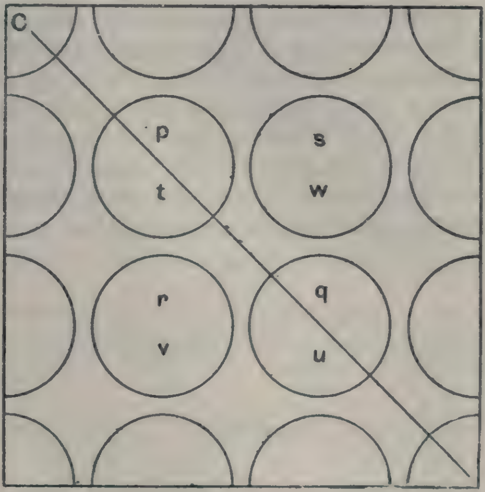
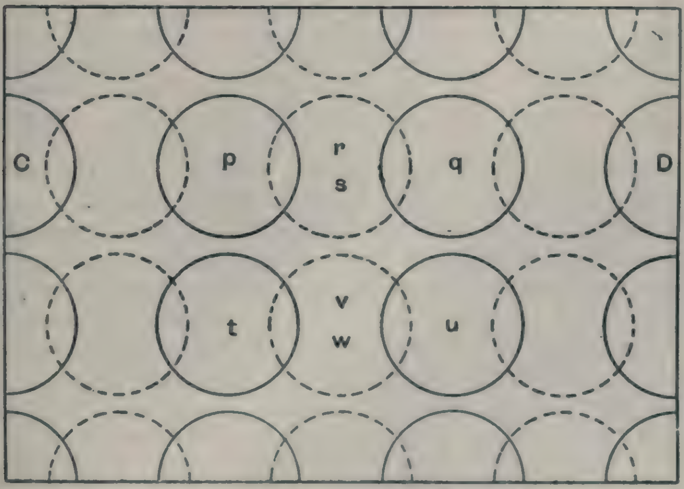


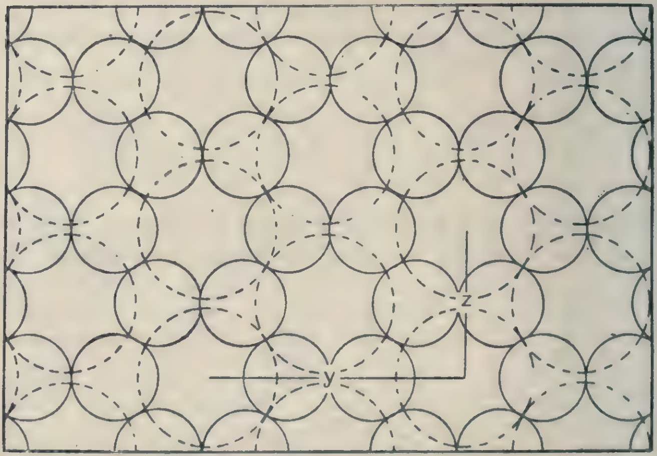
Fig. 16.



The process by which the present assemblage can be derived from that of methane, and also the converse, by which the former can be converted into the latter, are applications of the second geometrical property of close-packed homogeneous assemblages.

It remains to indicate the manner in which close-packing can be established in the assemblage of Figs. 13 and 14, that is to say, the way in which the assemblage can be caused to occupy the minimum space as the result of an adjustment which does not involve remarshalling. The requisite deformation will be understood by considering its effects on the system; these are indicated in Fig. 17, which represents one double layer of the two kinds of spheres, and in Figs. 18 and 19, which are projections of the altered assemblage on two planes at right angles to one another. For the sake of clearness, the hydrogen spheres are omitted from Fig. 18.

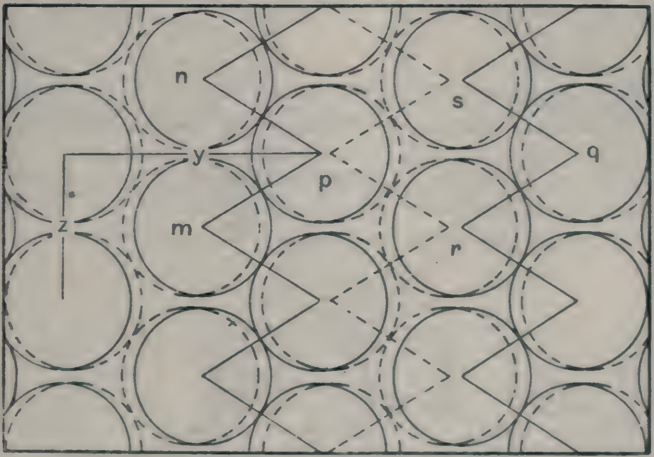
Fig. 17.



The symmetrical adjustment which increases the closeness of the packing brings the members of the rows of carbon spheres shown in Fig. 13 alternately into contact and further apart, as indicated in Figs. 17 and 18; thus a carbon sphere, such as p, makes contact only with m and n, and draws away from r and s. The sequence of making contact and moving further apart alternates in consecutive layers of the form shown in Fig. 17, so that these layers now have two distinct projections on the same area of Fig. 18; the latter diagram thus shows two alternating sets of carbon spheres, those indicated in continuous lines, and those in dotted circles, in place of the one set shown in Fig. 13. This alternation results in the formation, in each of the planes projected on Fig. 18, of zigzag strings of carbon spheres in contact and of indefinite length, the zigzag strings in one plane of the assemblage being located from the positions of others in the same plane or of those in the next neighbouring planes by some simple symmetrical operation such as that about a centre of symmetry; the zigzag strings in one plane do not lie immediately beneath or above those in the next plane.

The assemblage of Figs. 17, 18, and 19 represents the general methylene assemblage, and is to be regarded as an arrangement having the empirical composition CH_2, which constitutes the open-chain portion of a normal paraffin. By dividing the zigzag strings into fragments of suitable length by the introduction of pairs of hydrogen spheres at appropriate intervals, it may be converted, as is shown below, into an assemblage of molecular aggregates representative of any particular normal paraffin. The existence of this correspondence between the feature of close-packed assemblages just described and the observed fact that, in the normal paraffins, the chains of methylene radicles connecting the terminal methyl groups exhibit behaviour which warrants the representation of the normal paraffins by the general formula $CH_3{\cdot}[CH_2]_n{\cdot}CH_3$, is worthy of note.

FIG. 18.



It has been shown in previous papers that the configurations assignable, in accordance with the crystallographic evidence and with the theory of homogeneous close-packing, to numerous organic substances is in entire accord with some features of the chemical behaviour of such compounds. Before proceeding to employ the configuration arrived at for the general methylene chain, $\cdot[CH_2]_n\cdot$ in the production of assemblages representing the normal paraffins for comparison with the chemical facts and crystallographic evidence, it is therefore desirable to consider stereochemical features of the chain, $\cdot[CH_2]_n\cdot$, as now presented. Any such continuous chain separated from the whole assemblage presents the plan and elevation shown in Figs. 20 and 21; a rough perspective view of a fragment of the indefinitely prolonged chain is given in Fig. 22. It will be seen that each carbon sphere is directly attached to two other carbon spheres and to two hydrogen spheres, and that the plane containing the centres of the three carbon spheres is perpendicular to the plane drawn through the centres of the two hydrogen spheres and that of the carbon sphere which they touch. Further, it will be

FIG. 19.

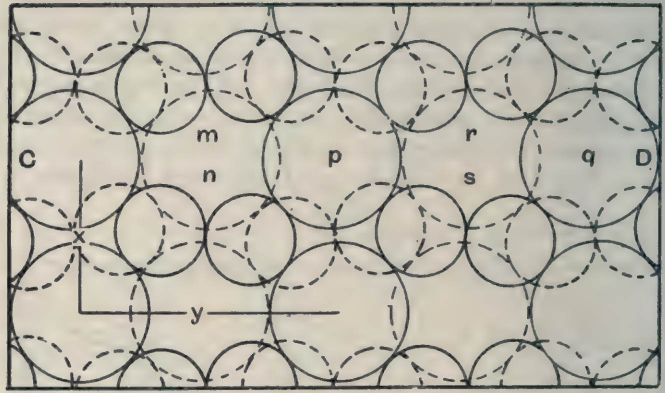
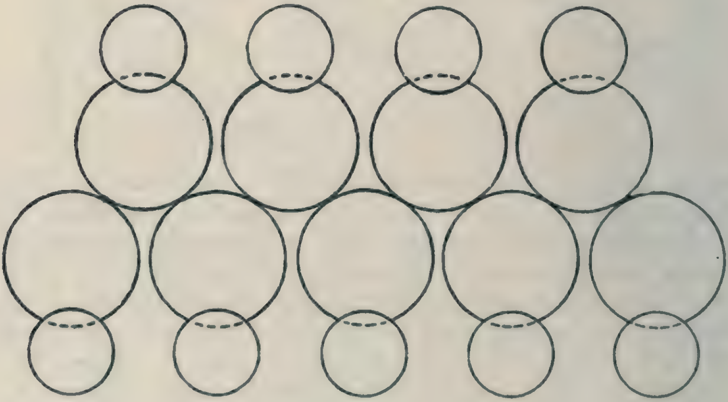


FIG. 20.



seen that by joining the four points of contact made on each carbon sphere, two by hydrogen and two by carbon spheres, a tetrahedron results. Since these are the essential features of the environment of any carbon atom of the chain in a normal paraffin, as summarised by the theory of van't Hoff and Le Bel, it follows that the configuration for the chain deduced above is in accordance with the chemical facts. In this connexion, it is interesting to recall the interpretation usually put on the important fact of the persistence of the tetrahedral arrangement of links from term to term of the series of assemblages representing the normal paraffins. Adopting the method employed by van't Hoff and Le Bel, the configuration of a string of methylene complexes which forms the backbone of a normal paraffin molecule is derived by first substituting carbon atoms for two of the tetrahedrally disposed hydrogen atoms of a methane molecule, preserving the tetrahedral disposition of the links, and then attaching two hydrogen atoms to each added carbon

FIG. 21.

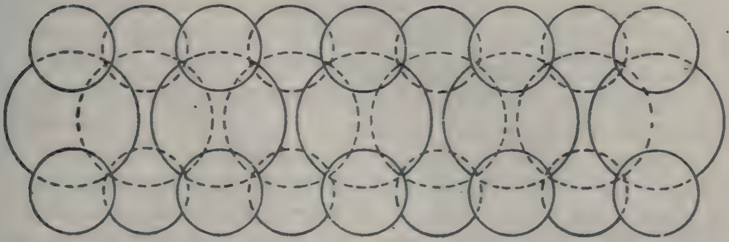
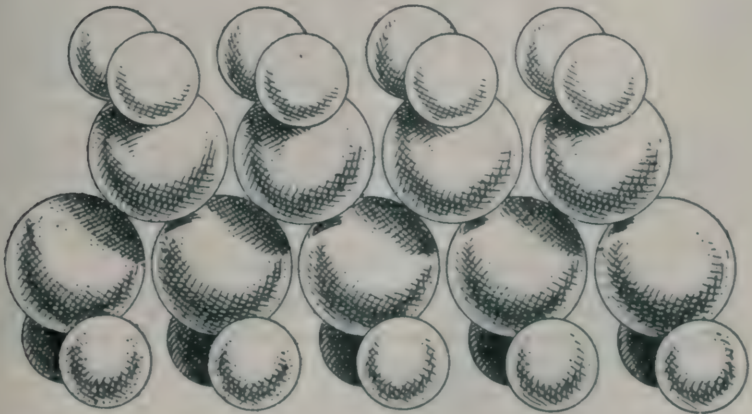


FIG. 22.



atom in such a way that the two outer methylene complexes thus formed are identical with the central one and identically related to it, while having the opposite orientation. The central portion, $\cdot CH_2\cdot CH_2\cdot CH_2\cdot$, of the propane molecule is thus arrived at. Arrangements proper for the representation of succeeding terms of the homologous series of paraffins are derived by repetitions of the same process.

The form of a group of methylene complexes reached in this way is quite definite and is that shown in Fig. 22; as the preceding argument has established, a number of the groups representing the same term of the series can be packed closely together so that the passage to closest-packed equilibrium involves but a quite trivial adjustment. When additional hydrogen spheres are inserted appropriately to complete the representation of a given paraffin, an assemblage results, as will be shown immediately, which displays the geometrical and dimensional properties appropriate to the crystal of the substance concerned.

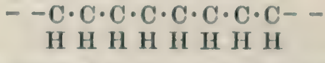
It is easy to demonstrate that the persistence of the tetrahedral type of arrangement is a geometrical consequence of substitution effected in accordance with the second geometrical property. For in carrying out such a substitution in a methane assemblage, the added carbon spheres are deposited in the hollows on the faces of the layers of the assemblage left vacant by the removal of hydrogen spheres, and consequently the incoming large spheres occupy practically the same situations with respect to the unsubstituted portions of the assemblage as were previously occupied by outgoing small spheres. Consequently, since the situations of the paraffin spheres give a tetrahedral arrangement of the contacts within a molecular group, this tetrahedral disposition of the contacts still obtains after the substitution. It is not suggested that the tetrahedral arrangement of the contacts will remain precisely regular.

The Ethane Assemblage.

The unit, shown in Fig. 22, of the general methylene assemblage of Figs. 17, 18, and 19 possesses the constitution of an indefinitely long string of attached methylene groups,

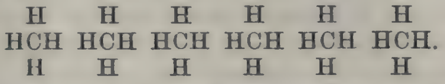
$$- - -CH_2\cdot CH_2\cdot CH_2\cdot CH_2- - -,$$

and is represented by the graphic formula:



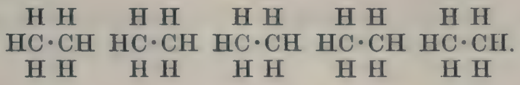
$$\begin{array}{c} \mathrm{H\ H\ H\ H\ H\ H\ H\ H} \\ - -\mathrm{C\cdot C\cdot C\cdot C\cdot C\cdot C\cdot C\cdot C}- - \\ \mathrm{H\ H\ H\ H\ H\ H\ H\ H} \end{array}$$

The comparison which has been made between the general methylene assemblage and the methane assemblage shows that if extra pairs of hydrogen spheres are introduced between succeeding carbon spheres, the resulting assemblage assumes the composition and constitution of methane, thus:



$$\begin{array}{cccccc} H & H & H & H & H & H \\ HCH & HCH & HCH & HCH & HCH & HCH. \\ H & H & H & H & H & H \end{array}$$

If, however, such pairs of hydrogen spheres are intercalated, not everywhere between succeeding carbon spheres, but intermittently at points homogeneously selected, the resulting assemblage should represent a normal paraffin homologous with methane. On introducing pairs of hydrogen spheres symmetrically at half the points indicated, the assemblage representing ethane should be produced, thus:



$$\begin{array}{ccccc} H\,H & H\,H & H\,H & H\,H & H\,H \\ HC\cdot CH & HC\cdot CH & HC\cdot CH & HC\cdot CH & HC\cdot CH. \\ H\,H & H\,H & H\,H & H\,H & H\,H \end{array}$$

It is desirable to confirm this deduction by an examination of the ethane assemblage, thus derived, in the light of the principal crystallographic evidence available; this is found in the data obtained by Gossner for the hexahalogen derivatives of ethane and for pentabromoethane (Trans., 1906, **89**, 1682). In the tabulated data for these substances it is convenient to double the ratio of c/b, and to state the equivalence parameters and axial ratios as in the appended table; the valency volume, $W=14$, is regarded as the molecular space unit, so that the linear unit employed for the equivalence parameters is the edge of a cube of unit valency volume. The closeness of the packing of the spheres is taken to be the same as that of the closest-packed assemblage of equal spheres:

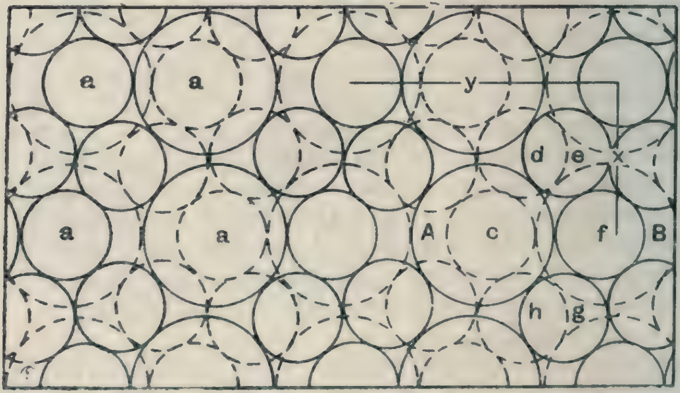
	$a : b : c$.	β.	$x : y : z$.
$CCl_3\cdot CCl_3$	0·5677 : 1 : 0·6320	90°	1·9255 : 3·3917 : 2·1435
$CBr_2Cl\cdot CCl_3$	0·5612 : 1 : 0·6342	,,	1·9086 : 3 4009 : 2·1520
$CBrCl_2\cdot CBrCl_2$	0·5646 : 1 : 0·6384	,,	1·9120 : 3·3867 : 2·1620
$CBr_3\cdot CBr_3$	0·5639 : 1 : 0 6284	,,	1·9205 : 3·4058 : 2·1403
$CHBr_2\cdot CBr_3$	0·5650 : 1 : 0·6236	91°19′	1·9282 : 3·4126 : 2·1281
	Mean for first four substances :		1·9166 : 3·3963 : 2·1494

In calculating the mean equivalence parameters, the four orthorhombic substances only have been considered, the monosymmetric pentabromoethane being excluded from the calculation.

It has now to be considered how the general methylene assemblage of Figs. 17, 18, and 19 can be converted into a close-packed assemblage of the dimensions represented by the above mean equivalence parameters, $x : y : z = 1·917 : 3·396 : 2·149$, by the intercalation of pairs of hydrogen spheres in the manner already indicated. The diameter of a univalent sphere is obtained in terms of the linear unit from the consideration that it is the face-diagonal of the cube outlined by joining the obtuse solid angles of the unit dodecahedron of a closest-packed assemblage of these spheres (Trans., 1907, **91**, 1181). Thus, if a be the diameter in question, $a/\sqrt{2}$ is the edge of the cube inscribed in the unit dodecahedron; the content of this cube is $a^3/2\sqrt{2}$, and that of the dodecahedron is equal to $a^3/\sqrt{2}$, which is taken as unity. Consequently, $a = 2^{\frac{1}{6}} = 1{\cdot}1225$, and since the volume of a quadrivalent sphere is four times that of a univalent one, the diameter of the former is $2^{\frac{2}{3}} \times 2^{\frac{1}{6}} = 2^{\frac{5}{6}} = 1{\cdot}7818$.

The sphere projections in the general methylene assemblage of Figs. 17, 18, and 19 are drawn to the scale thus indicated, and the dimensions indicated in these figures are, two of them, the values, $x = 1{\cdot}917$ and $y = 3{\cdot}396$, of the mean equivalence parameters in the table last given. On introducing between each pair of layers of the general methylene assemblage extra hydrogen spheres equal in number to the carbon spheres already present, the preservation of close-packing demands that the one pair shall shift upon the next pair, so that the projection of the two pairs now consists of four superposed sections, as depicted in Figs. 23, a and b.

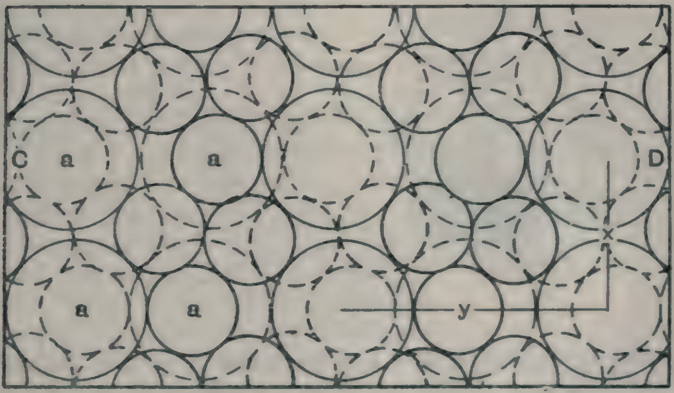
Fig. 23a.



In these diagrams, which, taken together, give a projection of the ethane assemblage, some of the intercalated hydrogen spheres are marked a; the dimensions, $x = 1{\cdot}917$ and $y = 3{\cdot}396$, are shown in the plane of the section. The packing is about as close as in the methane assemblage described above, and since the closeness of the packing is thus adhered to and the composition is that corresponding with ethane, the translation perpendicular to the plane of the section will necessarily have the corresponding value of $z = 2{\cdot}149$. Since the valency volume of the molecular unit is 14, and that of the terminal hydrogen spheres is 2, the dimension z of the methylene assemblage, as shown in Figs. 17 and 18, is six-sevenths of the z value just stated, and therefore equals 1·842; this is the value of z used in these diagrams. It is concluded from the above that the assemblage depicted in Fig. 23 is related to the general methylene assemblage in the appropriate manner, and has the dimensions indicated for ethane by the crystallographic data; the crystalline symmetry of the assemblage, when all the smaller spheres are identical in kind, is the orthorhombic symmetry exhibited by the hexa-halogen derivatives of ethane named in the table. It is, however, obvious that differences in kind occurring among the smaller spheres might have the effect of reducing the symmetry of the assemblage in the manner indicated by the existence of the monosymmetric pentabromoethane.

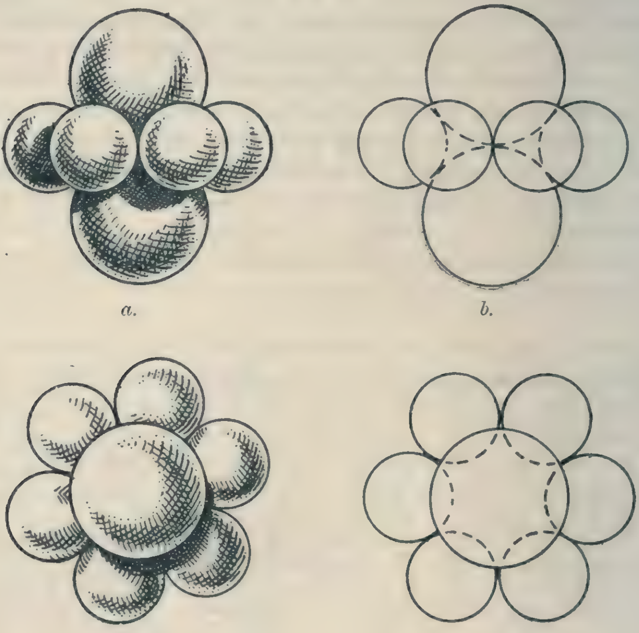
Lehmann has shown (*Molekular-Physik.*, 1888, **1**, 178) that hexachloroethane, C_2Cl_6, crystallises in an anorthic and a cubic form as well as in the orthorhombic form dealt with above; no measurements are available for the former modification, but it is instructive to deduce the assemblage representing the cubic form of the substance. In view of the close relationship which must exist between the orthorhombic and the cubic modifications of hexachloroethane, it is convenient to derive the assemblage for the latter from that of the former. The orthorhombic assemblage may, for purely crystallographic purposes only, be regarded as built up from a unit of the form shown in Fig. 24, *a*, *b*, *c*, and *d*, and consisting of two carbon spheres in contact having a circlet of six chlorine spheres placed round the neck produced between the two large spheres; the volumes of the two kinds of spheres, namely, 4 : 1, are such that when all the six small spheres touch the two larger ones, they very approximately form a continuous ring of small spheres in

FIG. 23*b*.



contact as shown in the diagrams. A geometrical unit of this kind is marked ABcdefgh in Fig. 23*a*, and presents in that diagram the aspect depicted in Figs. 25 *a* and *b*; it can be used in the manner described below for the construction of the assemblage representing the cubic modification of hexachloroethane.

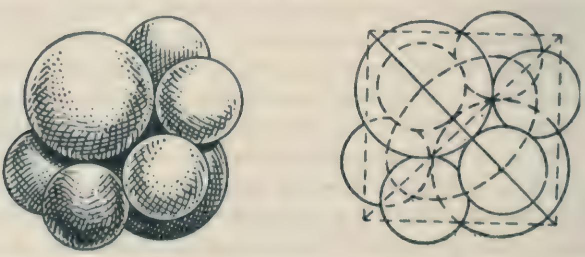
FIG. 24.



a. *b.*

c. *d.*

FIG. 25.



a. *b.*

The geometrical units referred to and figured occupy the valency volume, $W=14$, and can be fitted together in cubic symmetry so that their centre points lie at the centres of the cube cells of a cubic partitioning of space provided that the cube cells have the volume 14; the length of the cell edge should therefore be $\sqrt[3]{14}$, the scale previously used being adopted. The units are fitted into a system of non-intersecting trigonal axes of the kind already described (p. 2317), and in the following manner. In one cube cell the trigonal axis of which has the direction indicated by *a* (Fig. 5), place a geometrical unit group so that its centre is at the centre of the cube cell, and so that the centres of its two large spheres lie on the single trigonal axis of the cell; whatever the position of the small spheres, it is evident that their centres lie on a circle the centre of which is the point of contact of the two large spheres, and the plane of which is perpendicular to the trigonal axis of the unit. This circle is projected on one of the three face directions of the cube cells as an ellipse, as indicated in Fig. 25*b*. Geometrical units are now fitted in similar manner into the other cube cells of the system, due regard being paid to the preservation of the respective trigonal axes, *a*, *b*, *c*, and *d*, of the different cells of the partitioning.

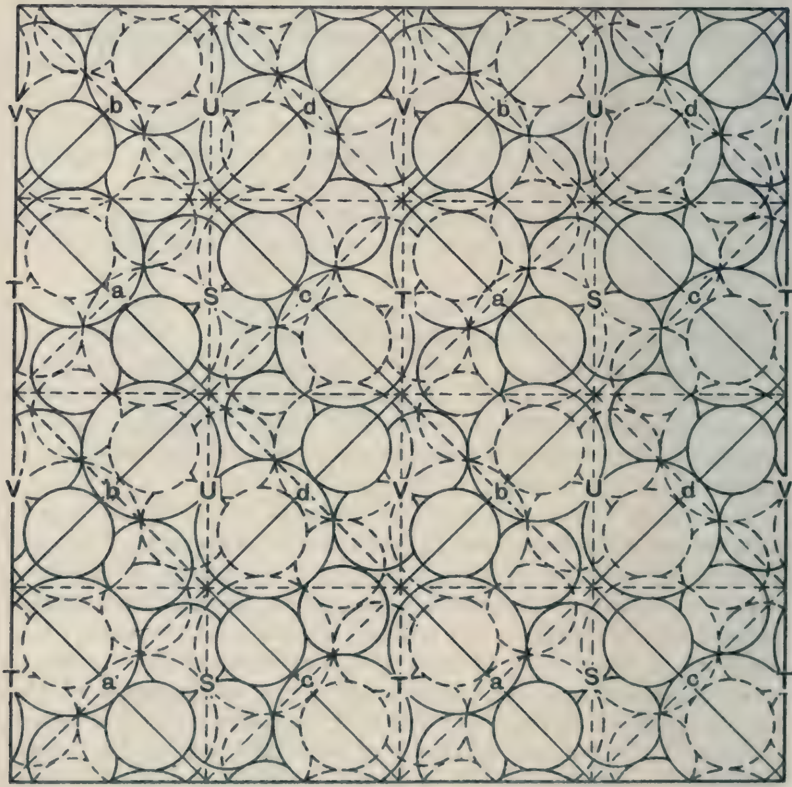
A single layer of the resulting system of cells with their contents is depicted in Fig. 26 as a projection on a cube plane; the projections of the trigonal axes are shown as continuous straight lines, and are lettered a, b, c, and d, in accordance with the convention previously adopted (Trans., 1907, **91**, 1183). Digonal axes of rotation pass through the assemblage perpendicular to the plane of projection at the points S, T, U, and V.

The precise position of the small spheres in the assemblage is deduced by reference to the digonal axes of symmetry. Thus the geometrical unit is so placed in the cube cell of the partitioning that the distance of the centre of one of its small spheres from a digonal axis is equal to the radius of the small sphere; this condition is practically fulfilled if the position of the circlet of small spheres is such that the centre of one of them lies at the highest point of the circular locus, the projection of this centre therefore falling at one extremity of the minor axis of the ellipse in which the circular locus is projected on the plane of a cube face. When one geometrical unit has been placed in position in the manner indicated, others can be similarly located with their centres at the remaining cell centres by carrying out the coincidence movements and operations with respect to the axes of the first selected cell. The type of symmetry is that numbered $2a_1$ in Barlow's list (*Zeitsch. Kryst. Min.*, 1894, **23**, 44).

It is evident from Fig. 26 that the spheres of the single layer of complexes fit closely together in the marshalling indicated, and, as the assemblage can be regarded as made up of such layers parallel to either of the three directions of the cube faces, it follows that the geometrical units employed can be fitted together in space in the manner indicated, and that the packing is very close.

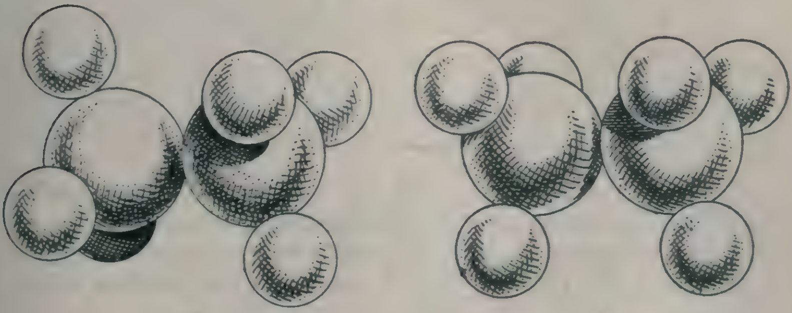
The geometrical unit which has been used in building up the orthorhombic and the cubic crystalline assemblage of hexachloroethane is, as before mentioned, merely used for constructional purposes, and is not to be regarded as possessing the configuration of the chemical unit or molecule. The possession of a larger mass of crystallographic data than is at present available should enable the configuration of the chemical molecule to be determined by a process of elimination. The various polymorphous forms of the different halogen derivatives of ethane must all consist of packed arrangements of units having the configuration of the ethane molecule; further, the latter must be derivable from the general

Fig. 26.



methylene assemblage by the symmetrical intercalation of spheres of unit valency volume in this assemblage, as already described. These conditions are fulfilled, not only by the geometrical unit used above, but also by groups of the composition C_2Cl_6 possessing a configuration such that the eight component spheres are centred at the apices of two tetrahedra so placed that an apex of the one is directed towards an apex of the other. The two kinds of unit of the structure thus distinguished possess the configuration of the ethane molecule as it has been deduced from the principles laid down by van't Hoff and Le Bel; rough perspective views of the chemical unit or molecule thus derived are given in Figs. 27 *a* and *b*.

FIG. 27.



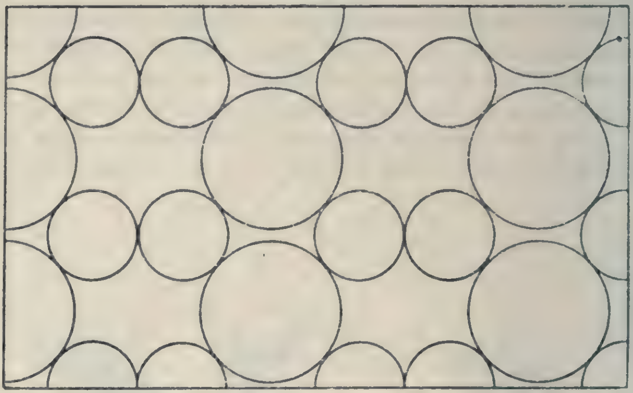
a. *b.*

It will be seen that the one may be derived from the other by rotating one-half of the unit through 180° with respect to the other half. The fact that these two configurations of unit, closely related by the mode in which one is convertible into the other, can be traced in the assemblage as depicted in Fig. 26, is of interest in connexion with van't Hoff's doctrine of the free rotation of a singly bound carbon atom.

An Alternative General Methylene Assemblage.

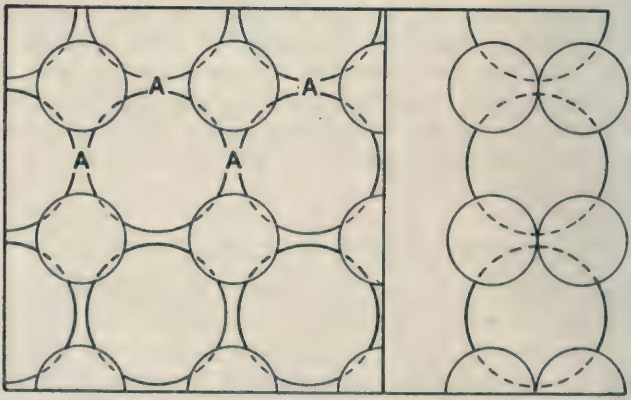
A simple method has been given above (p. 2333) for deriving an assemblage which can be geometrically partitioned into endless strings of the general form $n(CH_2)$, and it has been shown how the assemblages representative of the normal paraffins can be derived from this general methylene assemblage by the intercalation of hydrogen spheres. Examination shows, however, that by modifying the assemblage referred to by means of a particular kind of distortion, an alternative series of assemblages is obtained, in which the arrangement of the carbon and hydrogen spheres which form the methylene fragments is very nearly the same as before: this arrangement, like the first, is related to a number of crystallographic facts. The new kind of arrangement can be derived from the first by an adjustment or deformation which leaves each sphere with practically the same surroundings but which changes the general symmetry: the nature of the adjustment is as follows.

Fig. 28.



The large spheres of one layer (Fig. 28) in the unadjusted methylene assemblage of Fig. 14, when pressed together in the direction which is horizontal in the diagram, fall into a square arrangement; simultaneously, the smaller spheres, by movement on each other and on the large spheres with which they are in contact, are able to accommodate themselves to the altered form of the layer, and

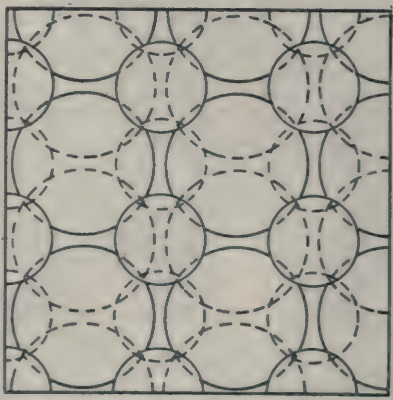
Fig. 29.



a. *b.*

can pack very closely into the hollows remaining after the change is made. The section of the assemblage shown in Fig. 28 thus becomes that shown in Fig. 29 *a* and *b*; the modified layer consists of a plane of the larger spheres in square arrangement with the smaller spheres sunk in the hollows on both of its faces; the small spheres touch each other in the plane drawn through the centres of the large spheres, as shown in Fig. 29*b*. Layers produced in this manner can be fitted closely together in such a way that the resulting assemblage is practically identical with that previously reached by compounding the layers in their other shape. In other words, the layers depicted in Fig. 29 are obtained from the general methylene assemblage of Fig. 14 if, instead of making the separation into layers parallel to the plane of Fig. 14, it is made parallel to the plane of projection of the same assemblage shown in Fig. 30. The plane of projection of Fig. 30 is at right angles to those of both Figs. 13 and 14; thus, in Fig. 31*a*, in which the arrangement is identical with that in Fig. 13, a plane perpendicular to the plane of the diagram, drawn through AB, gives the projection shown in Fig. 14, whilst a plane drawn through CD, also perpendicular to the plane of Fig. 31*a*, gives the section depicted in Fig. 31*b*.

FIG. 30.



The conversion of the general methylene assemblage depicted in Fig. 30 into that representing a normal paraffin is, as before, effected by intercalating hydrogen spheres, twice as numerous as the carbon spheres in a single layer, between consecutive layers of carbon spheres appropriately selected, the planes of these layers being parallel to the plane of projection of Fig. 30. It is seen from Fig. 29*a* that the principal hollows, which are of the kind marked A, in one of the surfaces of a layer are twice as numerous as are the carbon spheres of the layer; if therefore two such layers are appropriately placed together, a layer of hydrogen spheres twice as numerous as the carbon spheres of a layer can be closely fitted between them, each sphere occupying a principal hollow, such as A, in both the opposing faces. The combination of two layers of the composition CH_2 with the layer of hydrogen spheres thus fitted in between them, is shown projected in Fig. 32: the small spheres of the intercalated layer are indicated by double circles. In the assemblage representing a normal paraffin formed in this manner the hydrogen spheres added to a terminal layer of the form CH_2, and allotted to this layer, occupy the same positions in the face of the layer as they would if an additional CH_2 layer, of which they formed part, were added; this can be seen on inspection of the projection of a stratum of a paraffin assemblage of the form under consideration. The stratum represented in Figs. 31 *a* and *b* is that appropriate to normal butane,

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3;$$

corresponding with the four methylene radicles, CH_2, there are present four layers of large spheres in each stratum, as shown in Fig. 31*a*.

FIG. 31*a*.

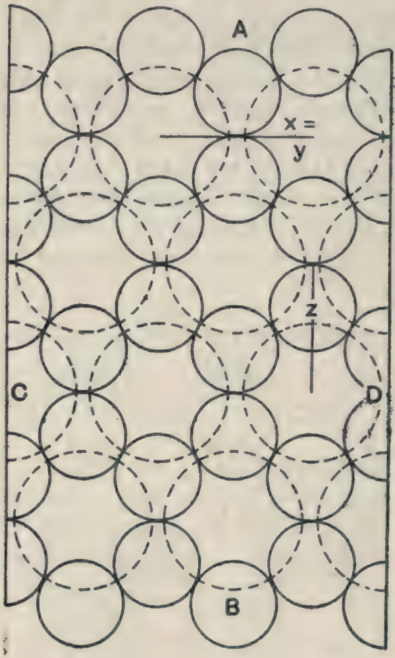
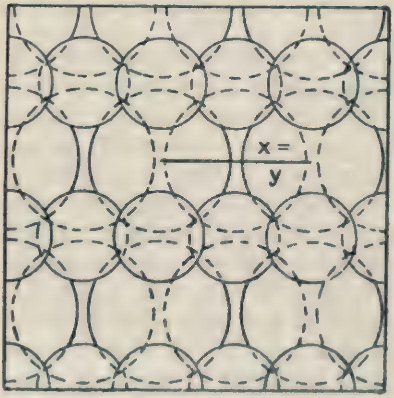


FIG. 31*b*.

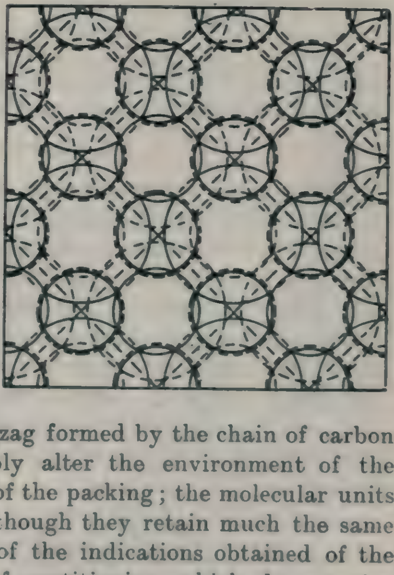


The centres of the terminal small spheres which have been introduced lie on two similar sets of digonal axes of the assemblage having two directions perpendicular to one another as indicated by the diagonal broken lines of Fig. 32; the identity of these digonal axes in the two directions involves the presence of screw tetragonal axes perpendicular to the planes containing the digonal axes. Thus, the assemblage of a normal paraffin in the modified form now described can present tetragonal symmetry; the orientations of the succeeding strata, each of which is composed of a certain number of layers of the composition CH_2 with the terminal hydrogen spheres added, will then differ by

90°. As remarked above, a section of a single stratum present in a butane assemblage is represented in Fig. 31.

That the marshalling of the assemblage of a normal paraffin, when of this altered form, is compatible with very close packing, is evidenced as before by the approach to a maximum of the number of contacts or close proximities round each sphere. Thus, each end carbon sphere of a chain is in contact with, or in close proximity to, six large spheres and fifteen small ones, together twenty-one, and each of the other large spheres is similarly environed by eight large and twelve small spheres, together twenty. Each terminal small sphere is environed by four large and four small spheres, and next to the terminal ones occur other small spheres immediately surrounded by five large and five small spheres: in the interior of the assemblage each small sphere is environed by six large and three small spheres. As before, the carbon spheres of a molecule containing several atoms form a zigzag string; the angles of the zigzag are, however, much more obtuse in the form of assemblage now under consideration. The relation between the latter, which may be called the tetragonal assemblage, and the orthorhombic form of assemblage previously described, is indicated by stating that whilst the marshalling of the methylene portion is the same in both, the one is obtainable from the other by a general distortion which alters the angles of the zigzag formed by the chain of carbon spheres, but does not appreciably alter the environment of the different spheres or the closeness of the packing; the molecular units are of a slightly altered form, although they retain much the same general configuration. In view of the indications obtained of the existence of alternative modes of partitioning, which do not give rise to observable tautomerism, in connexion with benzene (Trans., 1906, **89**, 1696), and of such alternative modes which furnish a mechanism for the occurrence of tautomeric and isomeric change, it is very possible that a paraffin derivative which occurs in one form of assemblage throughout one range of temperature would undergo conversion into the alternative form on entering a different range of conditions.

Fig. 32.



Crystalline Form of Halogen Derivatives of Homologues of Ethane.

It will be convenient now to discuss the rather sparse crystallographic data available for the halogen derivatives of the homologues of ethane, and to show that these data are very closely and very simply related to the two forms of assemblage described above. The whole of the available goniometric data are dealt with under this heading.

$\beta\beta\gamma\gamma$-Tetrabromobutane, $CH_3\cdot CBr_2\cdot CBr_2\cdot CH_3$, is dimorphous, and exists as a tetragonal and an orthorhombic modification, which have been measured by Fedoroff (*J. pr. Chem.*, 1890, [ii], **42**, 145). The tetragonal form has the axial ratio $a : c = 1 : 1\cdot28$; on stating this in the alternative tetragonal form of $a : c = \sqrt{2} : 1\cdot28$, and multiplying the value of c/a by four, the number of carbon atoms in the open chain, the ratio becomes, when stated in the more convenient orthorhombic form:

$$a : b : c = 1\cdot414 : 1\cdot414 : 5\cdot120.$$

The valency volume of this butane derivative is $W = 26$, and the equivalence parameters are thence calculated as:

$$x : y : z = 1\cdot929 : 1\cdot929 : 6\cdot985.$$

Since, in the tetragonal type of assemblage, the strings of carbon spheres which form the backbone of the molecules all have the same mean direction, symmetry would indicate that this is the direction of the axis c in the tetragonal crystal form now under discussion. The longer direction of the molecule having thus the direction of the parameter z, the dimensions of the fragment, CH_2, in the crystal structure should be the above x and y and the fraction, $6/26$, of the above length, z. The equivalence parameters of the fragment, CH_2, of the normal butane assemblage are thus calculated from the crystal form of the tetragonal modification of $\beta\beta\gamma\gamma$-tetrabromobutane as

$$x : y : z = 1\cdot929 : 1\cdot929 : 1\cdot612.$$

These values should represent translations in the tetragonal form of the general methylene assemblage; that they do represent such translations is shown by the manner in which they adapt themselves to the description of Fig. 31, in which they are marked. The orthorhombic modification of the substance is dealt with later (p. 2347).

The isomeric $\alpha\beta\gamma\delta$-tetrabromobutane,

$$CH_2Br\cdot CHBr\cdot CHBr\cdot CH_2Br,$$

is described by La Valle (*Ber.*, 1886, **19**, 572) as orthorhombic with $a : b : c = 0\cdot9776 : 1 : 1\cdot6820$, and is thus pseudotetragonal. Multiplying the ratio, c/b, by two, and calculating the equivalence parameters for the whole molecule with $W=26$, and for the fragment with $W=6$ in the same manner as before, the values are obtained as:

$x:y:z=1{\cdot}947:1{\cdot}992:6{\cdot}701$. With $W=26$.
$x:y:z=1{\cdot}947:1{\cdot}992:1{\cdot}546$. ,, $W=6$.

These values are not far removed from those obtained with the tetragonal isomeride; they suggest a slight spreading of the layers in the present instance as compared with the previous one, and a slight compensatory approximation of succeeding layers in the direction of the axis *c*. A stereoisomeride of this substance is considered below (p. 2348).

The tetrabromohexane of the constitution

$CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}CHBr{\cdot}CH_2Br$

is described by Negri (*Ber.*, 1889, **22**, 2498) as orthorhombic with $a:b:c=0{\cdot}3641:1:0{\cdot}3788$, and is also pseudotetragonal. On multiplying the length, *b*, by two, interchanging *b* and *c*, and calculating just as before the equivalence parameters for the whole molecule, with $W=38$, and for the fragment, CH_2, with $W=6$, the following values are obtained:

$x:y:z=1{\cdot}880:1{\cdot}956:10{\cdot}329$. With $W=38$.
$x:y:z=1{\cdot}880:1{\cdot}956:\ 1{\cdot}631$. ,, $W=\ 6$.

These values for the methylene fragment approximate closely to those derived from the two previous cases.

The three halogen derivatives just above discussed thus present the tetragonal type of assemblage; the following appear to exhibit the alternative orthorhombic type first described, of which the halogen derivatives of ethane previously referred to afford examples.

As already noted, $\beta\beta\gamma\gamma$-tetrabromobutane is dimorphous, and from Fedoroff's data for the orthorhombic modification Jaeger has calculated (Trans., 1908, **93**, 521) the axial ratios as $a:b:c=1{\cdot}8671:1:3{\cdot}478$. On multiplying the length *b* by four, the number of carbon atoms in the chain, interchanging *b* and *c*, and calculating the equivalence parameters for the whole molecule, with $W=26$, and for the methylene fragment, CH_2, with $W=6$, the following values result:

$x:y:z=1{\cdot}868:3{\cdot}479:4{\cdot}000$. With $W=26$.
$x:y:z=1{\cdot}868:3{\cdot}479:0{\cdot}923$. ,, $W=\ 6$.

From the mean values of the equivalence parameters for the halogen derivatives of ethane, namely, $x:y:z=1{\cdot}967:3{\cdot}396:2{\cdot}149$, with the valency volume, $W=14$ (p. 2335), we obtain for the methylene fragment, CH_2, with $W=6$, the values $x:y:z=1{\cdot}917:3{\cdot}396:0{\cdot}921$; the value of *z* here is half that of the *z* of Figs. 17 and 18. This set of values approximates closely to that calculated from the data for the orthorhombic $\beta\beta\gamma\gamma$-tetrabromobutane, and indicates that the latter substance affects a form of assemblage identical in type with the orthorhombic ethane derivatives.

An $\alpha\beta\gamma\delta$-tetrabromobutane, $CH_2Br{\cdot}CHBr{\cdot}CHBr{\cdot}CH_2Br$, stereoisomeric with that discussed above, has been described by Panebianco (*Ber.*, 1888, **21**, 1432) as crystallising in the monosymmetric system with $a : b : c = 2{\cdot}6348 : 1 : 2{\cdot}3338$, $\beta = 80°55'$. On transposing these axial ratios so that $\{101\}$ becomes $\{100\}$, and $\{\bar{1}01\}$ becomes $\{001\}$, the axial ratios are obtained in the form $a : b : c = 1{\cdot}6198 : 1 : 1{\cdot}8678$, $\beta = 82°58'30''$; in these values a is doubled and taken as b, c is taken as a, and b is multiplied by four and taken as c. The axial ratios are thus obtained in the form $a : b : c = 1{\cdot}8978 : 3{\cdot}2396 : 4{\cdot}000$, $\alpha = 82°58'30''$. The equivalence parameters for the whole molecule, with $W = 26$, and for the fragment, CH_2, with $W = 6$, are now calculated as before; the values obtained are:

$x : y : z = 1{\cdot}938 : 3{\cdot}316 : 4{\cdot}085$. With $W = 26$.
$x : y : z = 1{\cdot}938 : 3{\cdot}316 : 0{\cdot}943$. ,, $W = 6$.

The latter set of values also agrees well with that derived from the halogen derivatives of ethane, namely, with $x : y : z = 1{\cdot}917 : 3{\cdot}396 : 0{\cdot}921$.

The Secondary and Tertiary Paraffins.

The discussion of the configurations of the normal paraffins in the previous pages has revealed a singularly close correspondence between the customary method of representing the constitution of such substances and the conception of their configurations derived from the geometrical application of close-packing to assemblages of spheres of two volumes in the ratio of 4 : 1. It has yet to be shown that the correspondence extends to the secondary and tertiary hydrocarbons of the same series.

Tetramethylmethane (*ββ-Dimethylpropane*), $C(CH_3)_4$.

The most obvious method of arriving at the assemblage representing tetramethylmethane consists in replacing each hydrogen sphere in the methane assemblage by the methyl radicle, CH_3, in accordance with the second geometrical property; the discovery of the precise arrangement of the assemblage is, however, attended with much difficulty if this mode of procedure is adopted. Another method, which is more readily traceable, depends on the application of the first geometrical property to the methane assemblage, and may be thus described.

It has been pointed out that the four hydrogen spheres associated to form a close group in a methane assemblage belong to four different molecular groups, CH_4; if therefore a carbon sphere, which is quadrivalent, be substituted for a single close group of four hydrogen spheres, it will belong to, and will connect, four partial groups or radicles, CH_3, and thus give a composite group of the required composition, $C(CH_3)_4$. Consequently, if throughout the methane assemblage every fourth close group of the composition H_4, selected symmetrically, is removed, and a carbon sphere substituted, this being done in such a manner as to make the relation of the units so obtained to the assemblage as a whole identical, such an assemblage will furnish a possible solution. There are two ways of accomplishing this in a highly symmetrical manner, either of which would appear to be in harmony with the ascertained facts.

When the structure of the methane assemblage was under consideration, it was pointed out that the shape and orientation of the groups, H_4, influence the form of the skeleton framework composed of the carbon spheres, the reason of this being that the arrangement affected by these spheres must be such as gives the closest-packing of the groups in the cavities containing them; the substitution of single carbon spheres for some of the H_4 groups will, on the same principle, involve some slight modification of the skeleton framework of carbon spheres. The precise nature of this change is difficult to trace, especially in the absence of crystallographic data; for diagrammatic purposes it is therefore better, in each of the two solutions of the problem, to employ the simple arrangement of the carbon spheres in as high a symmetry as the marshalling which they present is capable of, without attempting to depict the exact equilibrium conditions ultimately attained.

The simpler of the two arrangements possible for the substituted carbon spheres has cubic symmetry. Thus, let the points of a certain cubic space-lattice indicate the centres of the carbon spheres of a methane assemblage; the centres of the cubes outlined by the system form a second similar space-lattice and mark the positions of the tetrahedral hydrogen groups. One-fourth of the groups can be selected for removal and substitution by additional carbon spheres in such a way that their arrangement is that of the unhatched cubes indicated in Fig. 33 *a* and *b*, which gives the two projections of the two sets of alternate layers. The alternative arrangement is a simple tetragonal one, and is shown in Fig. 34; this diagram is identical with Fig. 4, with the exception that every fourth cavity, symmetrically selected in tetragonal symmetry, is occupied by a carbon sphere. The newly introduced carbon spheres are shown as broken line circles, and are arranged contiguously in one of the three axial directions, namely, that perpendicular to the plane of the figure; the groups of hydrogen spheres, H_4, fill the strings of cavities marked A, which are not occupied by the added carbon spheres. Thus, the complete assemblage, much as in the case of benzene previously described (Trans., 1906, **89**, 1693), consists of continuous columns of carbon spheres in contact, the interstices between which are filled with groups of hydrogen spheres so arranged as to produce close-packing; the columns consist of square groups of four separated by single carbon spheres throughout.

Fig. 33*a*.

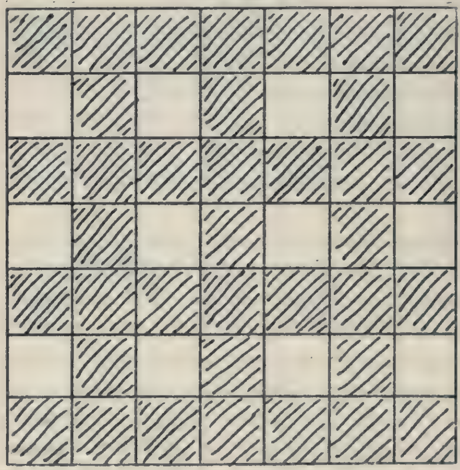
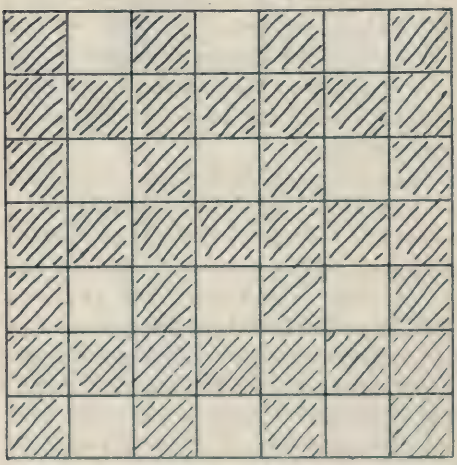


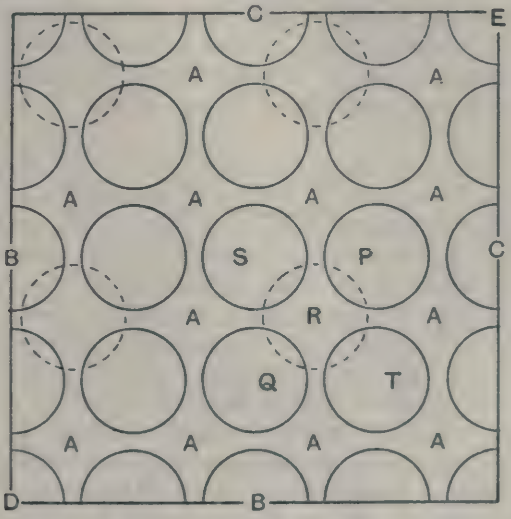
Fig. 33*b*.



In both the cubic and the tetragonal assemblage described, the most symmetrical way of partitioning the system of carbon spheres into groups of five is to make these groups tetrahedral with the substituted spheres at the centres. Thus, in Fig. 34, the sphere R can be associated with P and Q of the four above, and with S and T of the four below, the four spheres P, Q, S, and T thus presenting a tetrahedral arrangement about the sphere R. The disposition of the carbon spheres in the molecule of tetramethylmethane as thus derived is identical with that indicated by the theory of van't Hoff and Le Bel. The three hydrogen spheres attached to each methyl carbon atom will lie, as in methane, one in each of three out of four tetrahedrally situated cavities surrounding each methyl carbon sphere; the hydrogen spheres will follow, as closely as possible, the original arrangement prevailing in the methane assemblage.

Inspection of Fig. 34 shows that the tetragonal assemblage for tetramethylmethane, like the first described, must approximate closely to cubic symmetry. The correctness of the mode of arriving at the arrangement which is here adopted is confirmed by Jaeger's determination of the crystal form of the tetrabromo-derivative of the hydrocarbon, namely, $C(CH_2Br)_4$; this author has shown, as already indicated, that the substance is pseudo-cubic, being monosymmetric with the axial ratios, $a : b : c = 1{\cdot}0484 : 1 : 0{\cdot}9472$, $\beta = 90°45'$ (Trans., 1908, **93**, 520).

FIG. 34.



Trimethylmethane (iso*Butane*), $CH(CH_3)_3$.

It has been seen that the appropriate symmetrical intercalation or excision of methylene layers, CH_2, effected in the case of a given normal paraffin assemblage produces some other normal paraffin assemblage; similar operations applied singly or in succession to the tetramethylmethane assemblage just described are productive of other assemblages appropriate to secondary or tertiary paraffins. The principle involved in such operations may be stated as follows. A regular layer of spheres, so constituted as to form the unit layer of a closest-packed assemblage of spheres, for example, a methylene layer, forms a constituent of some closest-packed assemblage. It is then found (*a*) that the two parts of this assemblage obtained by the excision of this layer can close up and become closest-packed without any material rearrangement, and (*b*) that if, instead of removing this layer, the assemblage is divided so as to expose one of the faces of the layer, a second similar layer can be fitted on to this face and then the parts fitted up so as to form a closest-packed assemblage in which the added layer is intercalated.

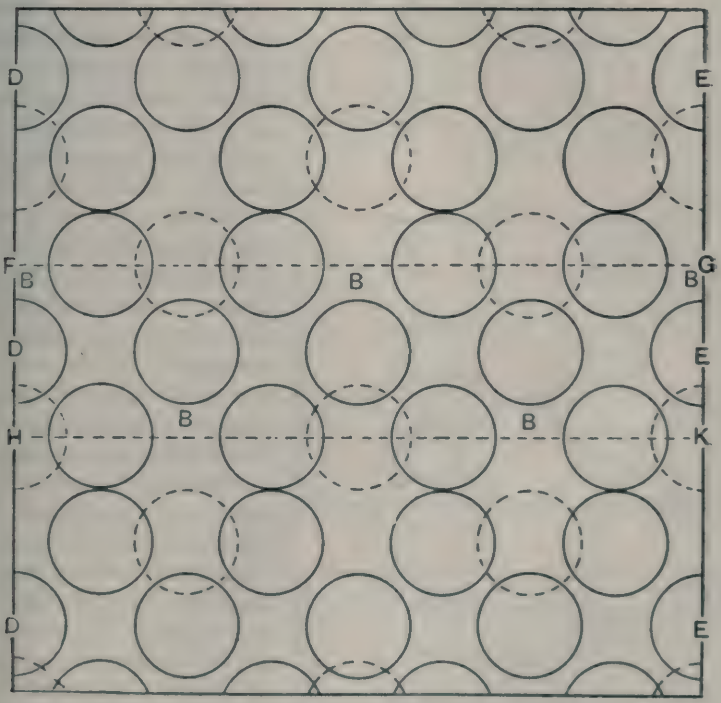
The application of this principle depends on the property of an assemblage composed solely of such identical layers that some translation brings the contour of the adjoining portion of the assemblage which is fitted against one side of a single layer to coincidence with the contour of the other side of this layer, coupled with the fact that close-packing involves a close similarity of contour between all the surfaces of different sphere combinations which display the common property of fitting closely on to the same surface.

For the present purpose, *iso*butane or trimethylmethane, $CH(CH_3)_3$, may be regarded as derived by the removal of methylene, CH_2, from the tetramethylmethane molecule. The possibility of performing this operation symmetrically on the tetramethylmethane assemblage, whether of the cubic form or of the tetragonal form represented in Fig. 34, constitutes a parallel between our method of formulation and the chemical relationship subsisting between the two hydrocarbons. The process is rather simpler as applied to the tetragonal form; this case may be described as follows.

One-fifth of the total number of carbon spheres in the tetramethylmethane assemblage are symmetrically removed, together with twice the number of hydrogen spheres, by withdrawing every fourth layer of the original carbon spheres taken parallel to a plane perpendicular to the diagram through a line DE in Fig. 34, together with the accompanying hydrogen spheres, and closing up the structure by bringing the exposed surfaces together. As the result of this operation, the skeleton assemblage depicted in Fig. 35 is obtained; it will be seen that, of the carbon spheres P, Q, S, and T, and the set of four, P_1, Q_1, S_1, and T_1, making up the eight carbon spheres which together enclose a substituted carbon sphere, only P, P_1, Q, Q_1, S, and S_1 survive, and that the new groups form two sets oppositely orientated in the resulting assemblage. In closing up the structure after removal of the methylene layer, a lateral shift is made, such a relative disposition of the opposing boundaries brought together being selected as brings the columns of carbon spheres at one boundary opposite to the strings of hydrogen spheres in the opposing boundary; this is possible because the central plane of the methylene layer in the original assemblage and the plane of the hydrogen spheres which becomes central in the modified assemblage are alike capable of functioning as planes of gliding symmetry. The approximation of the portions fitted together, or the space gained by the excision, is treated as dependent on the postulate that the group of four hydrogen spheres occupies the same space in the assemblage as one carbon sphere; it follows from this that the CH_2 layer occupies three-fourths of the space required by a CH_4 layer.

The method described indicates roughly the relation of the required assemblage to that of tetramethylmethane, but the character of the marshalling in the arrangement derived is imperfectly defined; still less is the precise nature of the crystalline symmetry exhibited. The absence of crystallographic data for the halogen derivatives of *iso*butane leaves the symmetry in doubt, but it is possible to assign to the marshalling of tetramethylmethane a very simple form, from which an equally simple one for trimethylmethane can be derived.

FIG. 35.



In the absence of crystal data, much latitude is presented for the shape taken by a given marshalling, and naturally the marshalling of an assemblage can be most readily investigated when in its simplest form. Although this form will not, in general, be the closest-packed one, it will approximate to the close-packed condition, and will display the property that every sphere will be in contact with, or in close proximity to, a large number of surrounding spheres. Now, the methane assemblage, without changing its general marshalling, can take the form depicted in Fig. 36 *a* and *b*; the simplest shape of the methylene layer, CH_2, as depicted in Fig. 11, can here be recognised. Each layer of molecules, CH_4, consists of the simple methylene layer with the additional hydrogen spheres symmetrically disposed in the same manner on both sides of it, as shown in the section *f*; the manner in which succeeding layers are fitted together in this simple marshalling is indicated by superposing *b* on *a* of Fig. 36. It must be clearly understood that the assemblage thus presented is not in its closest-packed form; it is a distortion of the closest-packed assemblage above described of such a nature as to simplify the internal symmetry without changing the marshalling. The methane assemblage, thus regarded, gives a configuration of the important radicle CH_2, which is

Fig. 36*a*.

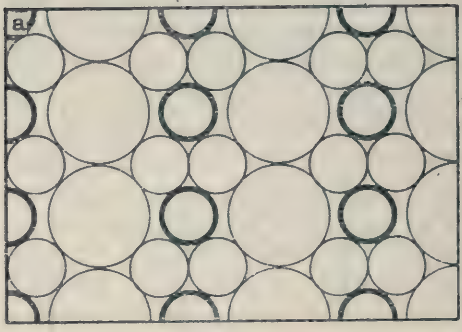


Fig. 36*b*.

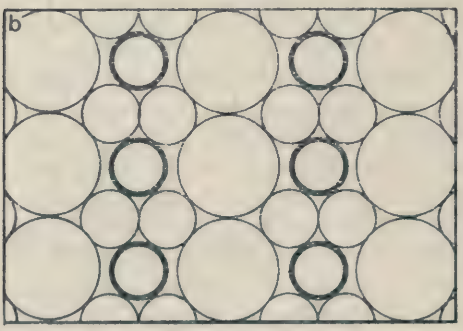
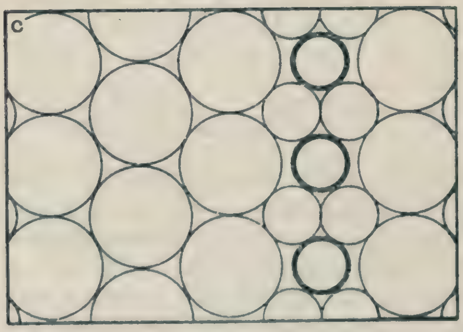


Fig. 36*c*.



entirely in harmony with the symmetrical properties expressed by the graphic formulæ of the hydrocarbons. When it is employed as the root methane assemblage, the marshalling of the compound under consideration, and that of other kindred compounds, can be readily traced, and will be seen to be in accordance with the graphic formulæ.

The first step is to derive the corresponding simple form of marshalling for tetramethylmethane; this corresponds with the tetragonal type of the compound above indicated, and may be regarded as produced from it by a distortion. The process of derivation from the methane assemblage just described consists in substituting strings of carbon spheres for one-fourth of the strings of groups of the composition H_4; as a result of this change, the arrangement shown by superposing *b* on *a* of Fig. 36 becomes that obtained by superposing *c* on *a* of this figure. The layers shown on the plane of the diagram are the same as those found parallel to a plane drawn through DE perpendicular to the plane of Fig. 34.

Fig. 36*d*.

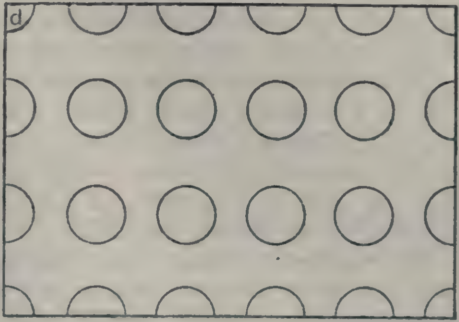


Fig. 36*e*.

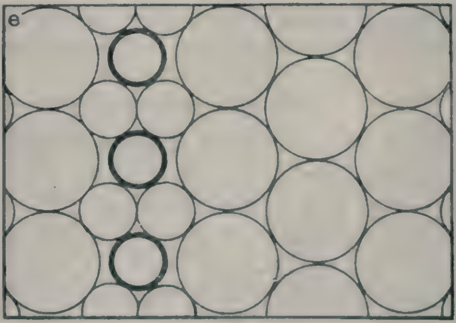
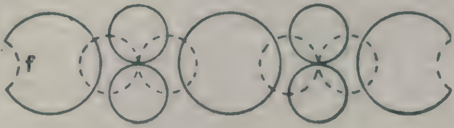


Fig. 36*f*.



The marshalling for trimethylmethane is obtained directly from that for tetramethylmethane by removing the central methylene portion from half the unsubstituted methane layers selected symmetrically and closing up the gaps, using the remnant hydrogen spheres in filling in between the parts of the assemblage which have to be fitted together after the excision. In the tetramethylmethane assemblage, layers of the composition $CC + CH_4$ (Fig. 36*c*) alternate with layers of the composition $2CH_4$ (Fig. 36*a*); the result of the excision described is to give a succession of sets of layers, $2CH_4 : CC + CH_4 : 4H : CC + CH_4$, etc., as represented roughly by superposing a, c, d, and e of Fig. 36.

The corresponding molecular unit is a combination of one carbon sphere from a layer *a* with the three carbon spheres of one of the two adjoining layers together with a due proportion of hydrogen spheres; the units are so constituted as to be all alike. With regard to the positions of the planes of gliding symmetry mentioned above, it is to be noted that in the tetramethylmethane assemblage the gliding plane is the median plane of layer *a*, and in the trimethylmethane assemblage it is the median plane of layer *a* or *d*; these planes of gliding symmetry can be traced in Figs. 34 and 35 respectively. As already intimated, the nature of the adjustment of this marshalling which would be productive of the precise crystalline form remains unidentified owing to the absence of crystal data.

The geometrical process by means of which the trimethylmethane assemblage can be converted into that of tetramethylmethane is analogous to the process of preparing tetramethylmethane by the action of zinc methyl on *tert.*-butyl iodide.

Dimethylethylmethane (iso*Pentane*), $(CH_3)_2CH{\cdot}CH_2{\cdot}CH_3$.

If, in the derivation of the *iso*butane assemblage from that of tetramethylmethane, a layer of the general methylene composition, CH_2, such as is excised from one side of the layer of tetramethylmethane complexes, is inserted in the symmetrical position on the other side of the layer, and the requisite shift of one layer on another made to close up the packing, the assemblage appropriate to *iso*pentane or dimethylethylmethane results. The added layer has thus to be inserted on one side of each layer marked DE in Fig. 35. The relative situations of the two layers, CH_2, thus placed together are indicated in Fig. 14; the relation of the composite layer formed to the remaining portion of the assemblage is shown in Figs. 34 and 35. The marshalling, as before, is represented in its simplest form.

Propane, $CH_3{\cdot}CH_2{\cdot}CH_3$.

If, in addition to the excision of the layers, DE, from the tetramethylmethane assemblage of Fig. 34 a set of layers, BAAC, parallel to them and symmetrically situated, is similarly removed and the exposed surfaces brought together as before, an assemblage is obtained which has the composition of propane. It is possible so to partition the assemblage thus obtained as to derive molecular units of the form already indicated for propane (p. 2334); this is most readily shown in connexion with the original tetramethylmethane assemblage of Fig. 34.

In the propane unit described in connexion with the normal paraffins, the central carbon sphere makes four tetrahedrally situated contacts with surrounding spheres, two with carbon and two with hydrogen spheres, and of the four tetrahedrally situated contacts of each end carbon sphere, one is with a carbon and three with hydrogen spheres. Now in the tetramethylmethane assemblage referred to, each central carbon sphere makes four tetrahedrally situated contacts with carbon spheres, and when the withdrawal of parallel strata occurs, two of the four outer carbon spheres and four hydrogen spheres are removed from each molecular group. And as the removal of the carbon spheres reveals hollows on the surfaces exposed, formerly occupied by these spheres, which, when the closing up takes place, are occupied by hydrogen spheres projecting from the opposing similar surfaces, it is evident that the central carbon sphere of each group is, after the process, surrounded by four spheres, two of each kind tetrahedrally arranged. Further, it can be shown that each end carbon sphere, as in the tetramethylmethane assemblage, has tetrahedrally situated contacts with a carbon sphere and three hydrogen spheres. Thus, the hydrogen spheres remaining of a methane stratum, from which the central CH_2 layer has been removed, are left embedded in the two faces exposed, half in each; they consequently retain the same positions relatively to the end carbon spheres of the group found in the stratum to which they are attached. The same is true of the hydrogen spheres centrally placed in the stratum containing the end carbon spheres. Consequently, each end sphere of a group has the same tetrahedrally arranged contacts with a single carbon sphere and three hydrogen spheres after the excisions are made, just as it had before. It is therefore established as above stated that the two propane assemblages, that of the ordinary paraffin structure and that derived from the tetramethylmethane assemblage, can be partitioned into unit groups of the same form; in other words, they are polymorphous arrangements of the same molecular groups. The geometrical process, inverse to that indicated above, by means of which the second kind of propane assemblage can be converted into that of tetramethylmethane, is analogous to Friedel and Ladenburg's conversion of ββ-dichloropropane, $(CH_3)_2CCl_2$, into tetramethylmethane by the action of zinc methyl.

The graphic formulæ for all the hydrocarbons of the general molecular composition C_nH_{2n+2} can be derived from those of methane, trimethylmethane, and tetramethylmethane by the introduction of methylene groups, CH_2, into the formulæ in all the ways consistent with the quadrivalency of carbon. It has been shown in the foregoing pages that close-packed assemblages of the general composition of the paraffins can be constructed which correspond in constitution and configuration with the normal hydrocarbons of the series; it has also been shown that other assemblages may be derived which possess geometrical properties exactly representative of the simple secondary and tertiary paraffins by means of simple substitution processes which closely parallel the modes of preparation of these hydrocarbons. The mode in which the geometrical substitutions are made renders it clear that similar operations appropriately performed will lead to the production of an assemblage corresponding in constitution with any primary, secondary, or tertiary paraffin. The conclusion must thus be drawn that the continued prosecution of the method described for deriving assemblages representing the paraffins must lead to a complete parallel between the possibilities of our geometrical method for interpreting atomic space arrangement and the variety of chemical processes of derivation which are so completely pictured with the aid of the ordinary graphic formulæ.

The Olefinic Hydrocarbons.

The results obtained by means of the above method of deriving close-packed assemblages, which represent in composition, constitution, and configuration all the primary, secondary, and tertiary paraffins, have been shown to accord with all the available goniometric data; although this evidence is small in amount, it appears to be of a very direct character. The assemblages for the normal paraffins are characterised by being built up wholly from the general methylene assemblage by the intercalation of additional hydrogen spheres in appropriate ways. It will now be shown that the reverse process, namely, the removal of hydrogen spheres from the general methylene assemblage, gives rise to a geometrical feature corresponding with the element of chemical constitution described as an ethylenic double bond. By the application of this process of excision to paraffinoid assemblages, fresh assemblages can be derived representing all the open-chain olefines of the general composition C_nH_{2n}, and it will further be demonstrated that peculiarities of configuration, which arise naturally during the process, represent the properties associated with the *cis*- and *trans*-isomerism of certain ethylene derivatives.

The formation of an olefine may be represented by the chemical operation of removing two hydrogen atoms from one terminal carbon atom of each of two paraffin molecules, and allowing the two bivalent radicles thus obtained to condense, forming a hydrocarbon molecule containing an ethylenic double bond; this corresponds with the production of ethylene by the action of copper on methylene iodide, and may be thus formulated:

$$CH_2I_2 - 2I + CH_2I_2 - 2I = CH_2{:}CH_2.$$

It has been shown that the orthorhombic and the tetragonal forms of the general methylene assemblage are capable of interconversion

Fig. 37*a*.

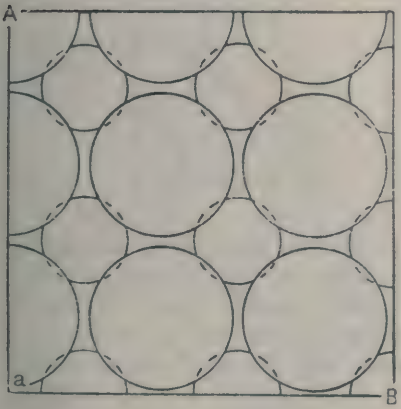
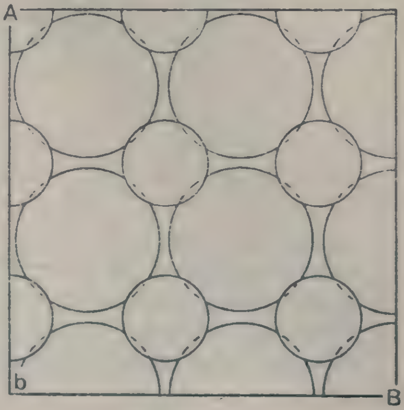
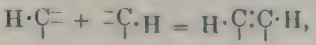


Fig. 37*b*.



by means of simple adjustment without any violent rearrangement. The described process of excision may be applied to either form, but the tetragonal one lends itself the more readily to its application; it is the one the employment of which leads to a result that can be checked by crystallographic data, whilst that of the orthorhombic form at present does not. The application of the process to the tetragonal form of the general methylene assemblage alone is given here; the treatment of the other form is not attempted, first, because it is not at the moment of practical importance, and secondly, because the first step in the derivation of an olefinic form from an orthorhombic paraffinoid form may possibly consist in the passage of the latter to the tetragonal form.

The configuration of the ethylenic grouping, as it presents itself in a homogeneous close-packed assemblage, is deduced by removing from a face of each of two composite layers, CH_2, of the general methylene assemblage of the tetragonal form, the small spheres lying in the hollows of the face, and by then keying together the two faces thus laid bare. The process itself parallels that which may be thus formulated:



$$H\cdot\underset{|}{C}{=} + {=}\underset{|}{C}\cdot H = H\cdot\underset{|}{C}{:}\underset{|}{C}\cdot H,$$

and is depicted in Fig. 37 *a* and *b* by superposing *b* on *a*; the section of the resulting assemblage of radicles through a line AB is given in Fig. 37*c*; it is concluded that the presence of such a double stratum as this is characteristic of an olefine. The only addition requisite to the stratum just described to produce from it the arrangement for ethylene is the appropriate insertion of spheres of valency volume 1 at each of its faces in the manner already described in connexion with the normal paraffins; the close-packed assemblage composed of the strata thus completed is obtained by arranging a succession of the strata of Fig. 37*c* with a layer of the small spheres between each of them, such as is shown in Fig. 37*d* (compare Fig. 32). In view of the comparative simplicity of this process, it will be convenient at once to demonstrate its application to a specific case in which a slight complicating adjustment accompanies the formation of the assemblage.

Fig. 37*c*.

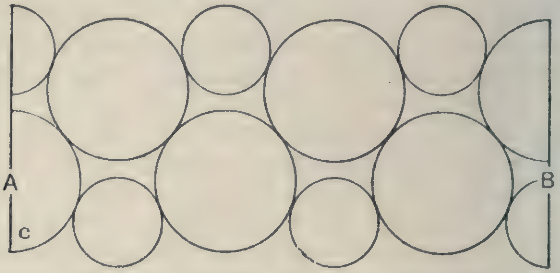
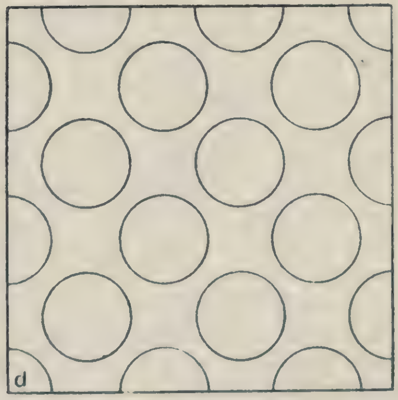


Fig. 37*d*.



Jaeger has described tetraiodoethylene, C_2I_4, as crystallising in the monosymmetric system with

$$a : b : c = 2{\cdot}9442 : 1 : 3{\cdot}4387,$$

$\beta = 70°44'30''$ (Trans., 1908, **93**, 523). In this description it is convenient to change the indices 001, $\bar{1}01$, $\bar{2}01$, $\bar{1}11$, and 100 to 100, 203, 001, 263, and $\bar{2}03$ respectively; the introduction of the factor three in this connexion seems permissible in view of the pronounced pseudohexagonal character of the compound, and as a result of the change the indices become more symmetrically distributed, although numerically somewhat more complicated. The axial ratios are then obtained in the form:

$$a : b : c = 1{\cdot}0891 : 1 : 0{\cdot}7360\ ;\ \beta = 84^\circ 3'\ ;$$

whence the equivalence parameters are calculated, with $W = 12$, as:

$$x : y : z = 2{\cdot}689 : 2{\cdot}469 : 1{\cdot}817\ ;\ \beta = 84^\circ 3'.$$

The assemblage appropriate to tetraiodoethylene, and also therefore to ethylene itself, is constructed on the basis of these values in the following manner. Carbon spheres are arranged in square order so as to be equidistant in the same plane, and nearly in contact, as in the general methylene assemblage of tetragonal form depicted in

FIG. 38*a*.

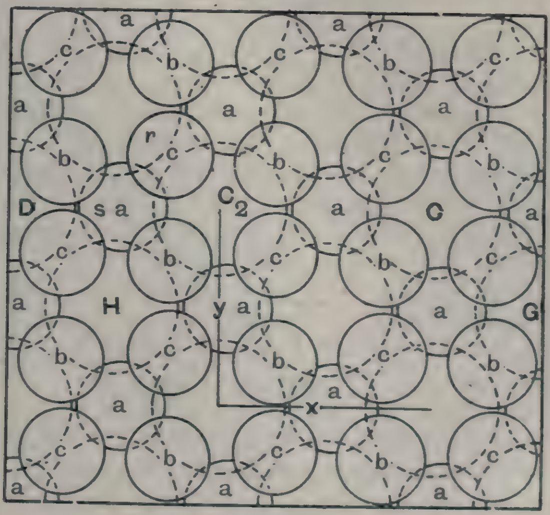


FIG. 38*b*.

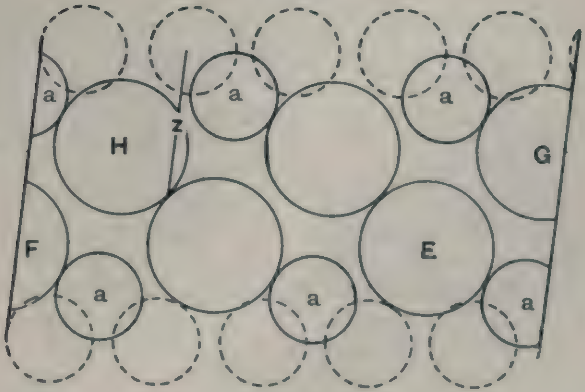


Fig. 29; the squares are then converted by a distortion into rhombs, the diagonals of which are in the ratio of $x : y$. The arrangement and dimensions of the system thus produced are indicated by the large circles of Fig. 38*a*. On one face of the layer of carbon spheres are now placed spheres of volume 1, representing hydrogen or iodine,

FIG. 39*a*.

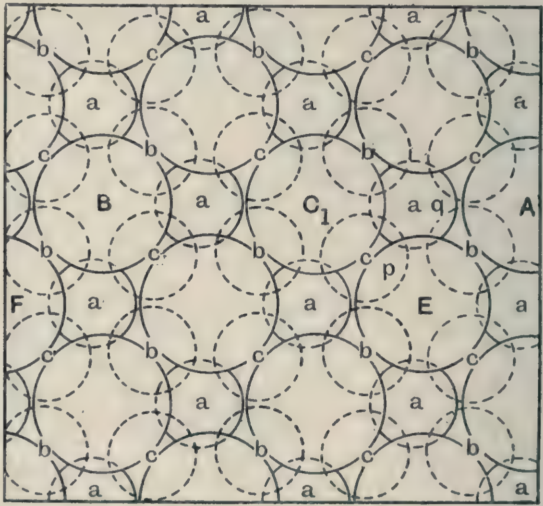
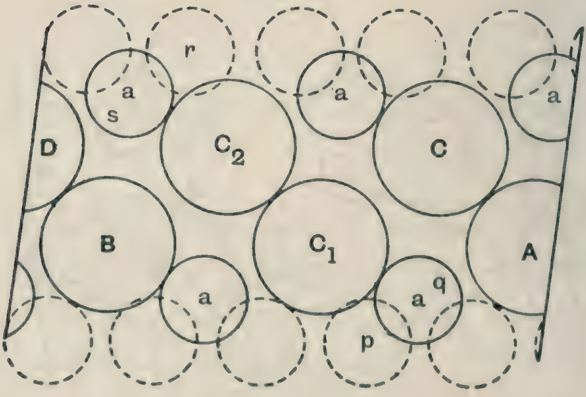


FIG. 39*b*.



one in each of the hollows. If the arrangement of the large spheres were a square one, each small sphere would touch four large ones, as shown in Fig. 37; as it is, each small sphere makes but three contacts, and symmetry requires that these shall be such that the centres of the small spheres display the same relative arrangement as the large ones, and are thus equidistant. Their situations are indicated by the circles marked *a* in Fig. 38*a*. The principal hollows now present on the face of the composite layer to which the spheres *a* have been added are just twice as numerous as the carbon spheres; they are next occupied symmetrically by other spheres of volume 1, as shown by the circles *b* and *c*. The block thus obtained can be regarded as consisting of three layers of spheres, one of large and two of small ones.

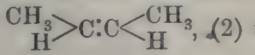
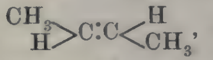
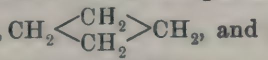
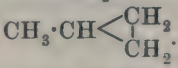
A second block of spheres similar to the first is now formed and the two blocks put together, so that the faces on which no small spheres have been placed fall together and key into one another, each large sphere of one block making contacts with three large spheres of the other block. Three contacts of large spheres are so made that the shift of the large spheres on the face of the block has the opposite direction to the shift of the small spheres, *a*, first placed on the other face. The relative situations of the two blocks are shown by superposing Figs. 38*a* and 39*a*, when it is seen that the system formed has digonal axes parallel to the direction *y* passing through points of contact of carbon spheres; sections of the double layer of two blocks by two planes perpendicular to those of Figs. 38*a* and 39*a*, through the lines AB, CD and EF, GH respectively, are shown in Figs. 38*b* and 39*b*. Double blocks of the form thus obtained are fitted together in such a manner that the end layer of small spheres, *b* and *c*, of one block serve as the end layer of the next double block; thus, if the spheres *b* are allotted to one double block, those marked *c* are to be allotted to the adjoining one.

The composition of the completed assemblage corresponds with that of ethylene or tetraiodoethylene, and its dimensions, *x*, *y* and *z*, are the equivalence parameters above derived for the latter substance. It will be seen that the assemblage differs merely by a slight adjustment and a sheer equivalent to the angle $\beta = 84°3'$ from the more symmetrical one constructed to represent ethylene in which the carbon and hydrogen spheres are in square arrangement. It is interesting to note that the plane directions with the somewhat complex indices given above are found to be very important directions in the assemblage when their traces are drawn on the plan and section here given.

The fact of the limitation of the number of derivatives of the normal paraffins led van't Hoff to ascribe freedom of rotation to a singly bound carbon atom; a limitation of this kind does not obtain in the case of a doubly bound carbon atom, although the accepted graphic representation of the altered molecule and its derivatives are capable of a digonal rotation by means of which it could be represented. This discrepancy points to the loss of some symmetrical feature due to the presence of the double bond. An examination of the effect on a normal methylene assemblage of the removal of the double layer of hydrogen spheres and the closing of the gap, which, it is suggested, expresses the change referred to, shows that a deterioration of symmetry has supervened; strings of carbon spheres are not continued in the same planes across the plane at which the modification occurs, but a side shift or "fault" is necessitated in order that the two denuded surfaces may fit closely together. It is suggested that the existence of this break in the regularity of the strings of carbon spheres makes two different orientations equally available for the portion of an assemblage lying beyond the surface of modification; in other words, whilst in the case of a normal paraffin assemblage of the tetragonal form the addition of a layer, in order to give equilibrium, must be so performed that the joined layers have the same orientation, in the case where a double or ethylenic bond is present, it is equally favourable to equilibrium whether the two layers coming together have the same orientation or differ in orientation by 90°. The parallel which thus exists between the properties of close-packed assemblages and the occurrence of *cis*- and *trans*-isomerides amongst the derivatives of ethylene will be treated immediately in connexion with the isomerides of the composition C_4H_8.

It should be remarked that the existence of the alternative referred to for the attachment of an added layer is inoperative in the case of ethylene, and in the cases of compounds equally symmetrical, such as tetraiodoethylene; in all such cases the two resulting forms become identical, and thus indicate, as they should do, that there is but one kind of molecule. The alternative becomes operative, however, in some derivatives of this simple form, since partial substitution of the hydrogen spheres allows two kinds of partitioning to be discriminated which are not interchangeable without remarshalling. The effects of the presence of the structure represented by the ethylenic bond, as exhibited in cases of homologues of ethylene, will now be traced.

The Homologues of Ethylene.

After having traced a peculiarity of geometrical structure in a close-packed assemblage which corresponds with the double bond present in the ethylene molecule, it is desirable to ascertain whether the introduction of this geometrical feature into a paraffinoid assemblage leads to the production of the type of assemblage specifically associated with the presence of an ethylenic bond. For this purpose, it is convenient to consider the four butylenes, C_4H_8, which may be regarded as derived from butane and *iso*butane by the removal of two hydrogen atoms from the molecule; these substances are (1) *cis*-*s*-dimethylethylene,  $\begin{matrix}CH_3\\H\end{matrix}\!>C{:}C<\!\begin{matrix}CH_3\\H\end{matrix}$, (2) *trans*-*s*-dimethylethylene,  $\begin{matrix}CH_3\\H\end{matrix}\!>C{:}C<\!\begin{matrix}H\\CH_3\end{matrix}$, (3) ethylethylene (butylene), $CH_3{\cdot}CH_2{\cdot}CH{:}CH_2$, and (4) *as*-dimethylethylene (*iso*butylene), $(CH_3)_2C{:}CH_2$. Further, in order that the possibilities of close-packing under the specified condition of unit composition may be exhausted, as also those of isomerism of the molecular composition C_4H_8, it will be convenient to discuss the assemblages representative of the remaining two hydrocarbons of the latter composition, namely, (5) tetramethylene (*cyclo*butane),  $CH_2\!<\!\begin{matrix}CH_2\\CH_2\end{matrix}\!>\!CH_2$, and (6) methyltrimethylene (methyl*cyclo*propane),  $CH_3{\cdot}CH\!<\!\begin{matrix}CH_2\\|\\CH_2\end{matrix}$.

It will now be shown that the process of excising hydrogen spheres which has been applied above for the purpose of deriving the assemblage representing ethylene can be applied in three different ways to the normal butane assemblage; these lead to the production of three distinct assemblages, which represent the butylenes, numbered (1), (2), and (3). A similar process applied to the *iso*butane assemblage leads to the formation of an assemblage, which represents the asymmetrical dimethylethylene, numbered (4). In connexion with the analogy existing between the geometrical mode of representation employed and the possibilities of chemical isomerism, it will be shown that these four methods of applying the process of excision are the only ones that lead to the production of the geometrical peculiarity of structure corresponding with the presence of an ethenoid double bond; three other modes of excision are, however, also applicable, two to the butane assemblage, and one to that of *iso*butane; all of these result in the formation of assemblages which do not contain the ethenoid peculiarity of geometrical structure. Of the latter assemblages, two are identical and represent methyltrimethylene (6), which is derived both from the butane and the *iso*butane assemblage; the remaining assemblage is that of (5), tetramethylene, and is derived only from the butane assemblage. Since assemblages representative of the four homologues of ethylene and the two polymethylenes, which constitute all the isomerides of the composition C_4H_8, are derivable from those representing the only two hydrocarbons of the composition C_4H_{10} by processes entirely analogous to the chemical methods of preparing the former hydrocarbons, strong confirmation is afforded of the general accuracy of the mode of formulation now put forward. These cases illustrate in a striking manner the geometrical property to which has been ascribed the persistence of the tetrahedral disposition of the atomic links when substitution occurs; they consequently throw light on the precision with which the ordinary formulæ indicate the number and nature of the isomerides obtainable in any particular case.

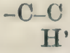
The three modes of excision applicable to the assemblage representing normal butane for the purpose of deriving assemblages representative of the butylenes (1), (2), and (3) are the following. In a stratum of the normal butane assemblage of the tetragonal form, four attached layers of the composition CH_2, and of the square configuration, are present; to each of the terminal faces of the block an appropriate set of hydrogen spheres has been added, as already explained (p. 2336). The stratum indicated is first divided at the median plane, so that each half consists of two layers of the form CH_2, to one of which an additional set of hydrogen spheres has been added. From the surface of each of the two halves exposed by the separation the small spheres are now removed, and the two halves are then refitted together, making the large spheres of one face fit into the hollows of the other; this operation may be performed in two ways, one being represented by superposing *b* on *a*, and the other by superposing *c* on *a* of Fig. 40. In these diagrams the groups fitted together are of the form  $-\mathrm{C}-\underset{\mathrm{H}}{\mathrm{C}}$, all the hydrogen spheres attached to the outer layer of carbon spheres—those representing the methyl hydrogen atoms—being omitted for the sake of clearness. The superposition of *b* on *a* gives the assemblage corresponding with *cis-s*-dimethylethylene, and that of *c* on *a* the assemblage for the *trans*-isomeride. No hydrogen spheres lie between the two denuded layers of carbon spheres fitted together as described, and the hollows

FIG. 40*a*.

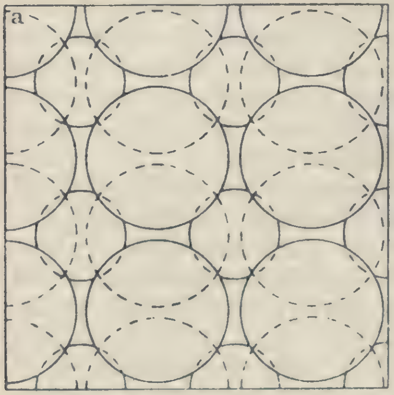
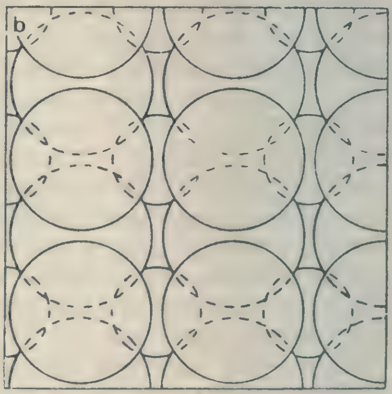
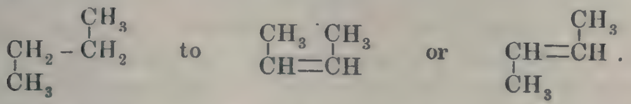


FIG. 40*b*.



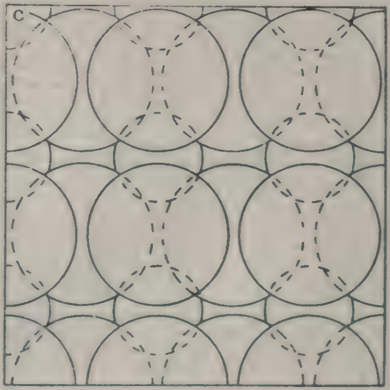
on the denuded surfaces from which the hydrogen spheres have been removed are now occupied by the carbon spheres of the opposing face. The geometrical operation which has thus been performed upon the normal butane assemblage may be roughly represented diagrammatically by the following scheme:



$$\begin{array}{l} CH_3 \\ CH_2 - CH_2 \\ CH_3 \end{array} \quad \text{to} \quad \begin{array}{l} CH_3\ \ CH_3 \\ CH{=}CH \end{array} \quad \text{or} \quad \begin{array}{l} CH_3 \\ CH{=}CH \\ CH_3 \end{array}.$$

The assemblage of (3), ethylethylene, is derived from that of normal butane by dividing the latter at the place of either the first or third linking so as to give as one segment a single layer of the form CH_2, with its additional small spheres attached to one face only, and, as the other segment, a block or stratum of three layers, CH_2, with the additional small spheres attached to one of its boundary faces. As before, the small spheres are removed from all the hollows of the two faces exposed by the separation, and the surfaces are then refitted; this operation can only be performed in one way without destroying symmetry, or rather, the two most symmetrical ways of fitting the strata closely together to produce a continuous assemblage give identical results.

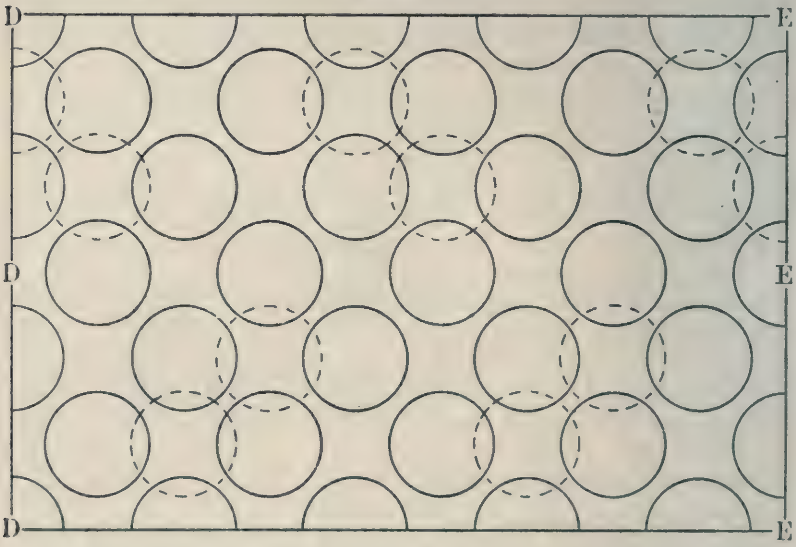
FIG. 40c.



The assemblage for *as*-dimethylethylene (4) can be obtained from that of *iso*butane, but is most conveniently derived from that of tetramethylmethane, $C(CH_3)_4$, already described (Fig. 34), by removing from the latter one-half of the layers which have the composition H_4C, namely, either those whose median planes pass perpendicularly to the plane of the diagram through all the diagonal lines BC, or those whose median planes pass through all the lines DE. On removing the strata thus indicated and then re-fitting the denuded surfaces, a general arrangement is attained of which the large spheres alone are represented in Fig. 41; in this figure the unremoved layers of the composition H_4C are marked DE.

The three modes of excision which do not lead to the production of the geometrical feature corresponding with the ethenoid double bond remain to be dealt with; that which yields the assemblage corresponding with (5), tetramethylene, $\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2}\\\mathrm{CH_2}\end{matrix}>\mathrm{CH_2}$, is next described. The assemblage for this hydrocarbon is derived from that of normal butane of the tetragonal form (Fig. 31) by removing the layers of hydrogen spheres which correspond with the terminal atoms in the paraffin chain, thus obtaining strata of the methylene form of assemblage, each consisting of four tetragonal layers of carbon spheres and the accompanying hydrogen spheres. Each stratum is next adjusted so as to bring its constituent carbon spheres close together in fours, as indicated diagrammatically in Fig. 42 *a* and *b*; the planes of these sections are perpendicular to those of the tetragonal layers. The grouping is so performed that each four tetragonal layers of carbon spheres and attendant hydrogen spheres furnish two layers of tetramethylene complexes, as indicated by *a* and *b*. A single tetramethylene complex, plan and elevation of which are shown in Fig. 43 *a* and *b*, consists of four large spheres in the same plane and eight small spheres, four in each of two planes parallel to and equidistant from the plane of the carbon spheres.

FIG. 41.



The two remaining modes of excision applicable as already intimated (*a*) to the butane and (*b*) to the *iso*butane assemblage, lead to the production of the same molecular unit, that which represents methyltrimethylene; the former is applied to the normal butane assemblage of the orthorhombic form in the following manner.

(*a*) Alternate layers of the small terminal spheres of the normal butane assemblage are removed as if for the purpose of condensing the strata in pairs so as to form strata of the normal octane

FIG. 42*a*.

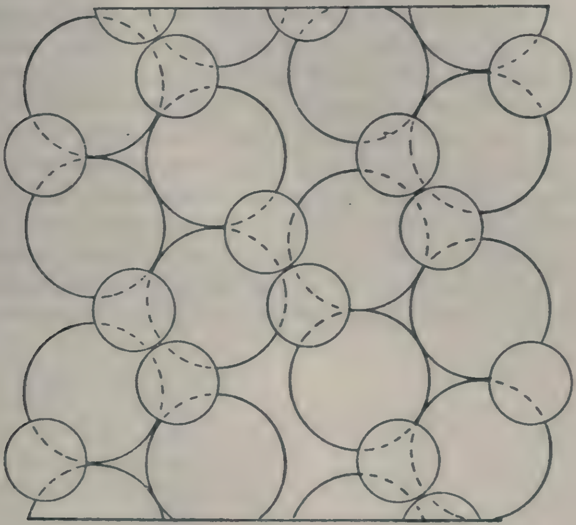
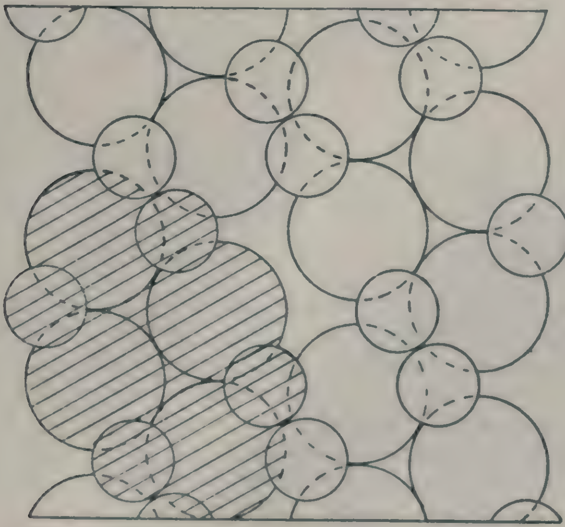


FIG 42*b*.



assemblage, and each mutilated butane stratum is divided symmetrically into blocks of the composition CH_3 and $3(CH_2)$ respectively. The latter blocks are next so adjusted that, as condensed together two by two, they form aggregates of trimethylene complexes arranged as is indicated by superposing *a* and *b* of Fig. 44; each stratum consists of six layers of large spheres as shown in the figure, and, as in the previous case, each small circle represents two spheres. Finally, one-half of the hydrogen spheres are removed symmetrically from the outer layers of the double stratum just described, and the outer layers are refitted to the CH_3 layers from which they were separated, the projecting carbon spheres of one face of the latter being allowed to fall into the hollows vacated by the hydrogen spheres last removed; simultaneously, the small spheres of the added CH_3 layers are adjusted for close-packing. The precise effect of the last process is difficult to trace, but its practicability is indicated by the facts that when the refitting has taken place, each sphere of the altered trimethylene layers is still immediately surrounded by the large number of spheres appropriate for very close-packing, and that no destructive deformation of the original CH_3 arrangement is necessitated. The refitting of the layers is represented by the equation: $3(CH_2) - H + CH_3 = CH_3{\cdot}CH{<}\begin{matrix}CH_2\\ | \\ CH_2\end{matrix}$, and the assemblage attained is, as indicated by its constitution, composed of trimethylene complexes, from each of which a hydrogen sphere has been removed, grafted on to modified methyl complexes.

FIG. 43*a*.

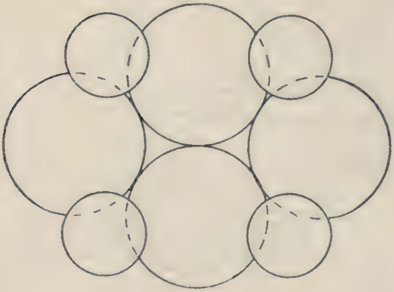
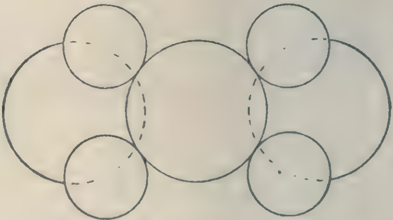


FIG. 43*b*.



(*b*) A different assemblage of the same trimethylene complexes is derived from that of trimethylene by an appropriate excision of hydrogen spheres in the manner next described. In Fig. 35, representing the arrangement of the carbon spheres in the trimethylmethane assemblage, cavities and portions of cavities, which lie between two planes of which the traces are marked FG, HK, are available for the reception of hydrogen spheres; the central entire cavities are each of the magnitude requisite for the reception of four hydrogen spheres, and the portions or half cavities have half this magnitude. Whilst maintaining the same configuration of the groups of four large spheres as is indicated in the figure, the two opposite sets are now allowed to approach until the cavities and portions of cavities afford only one-half the previous accommodation for hydrogen spheres; the effect of diminishing the accommodation offered by the cavities and portions of cavities to one-half the original amount is indicated in Fig. 45. Finally, without re-marshalling, such mutual adjustments are conceived as will adapt the various cavities between the large spheres to the close-packing of the appropriate numbers of hydrogen spheres; these adjustments will resemble, in general, those previously described in connexion with simpler cases.

FIG. 44*a*.

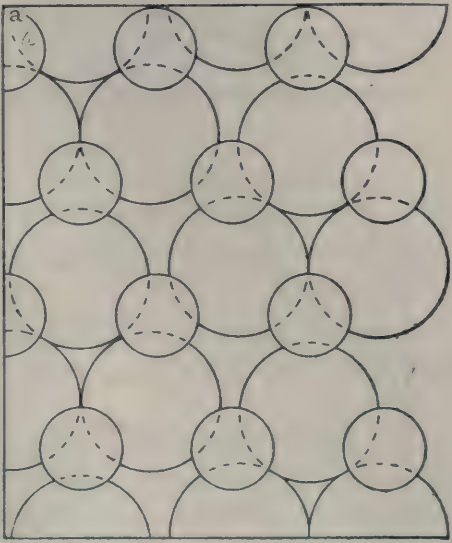
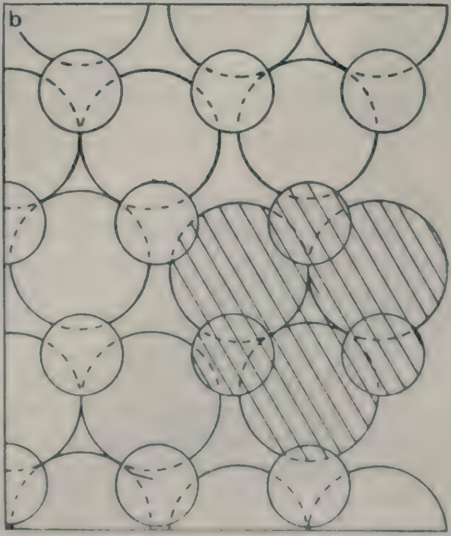
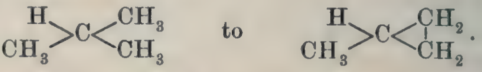


FIG. 44*b*.



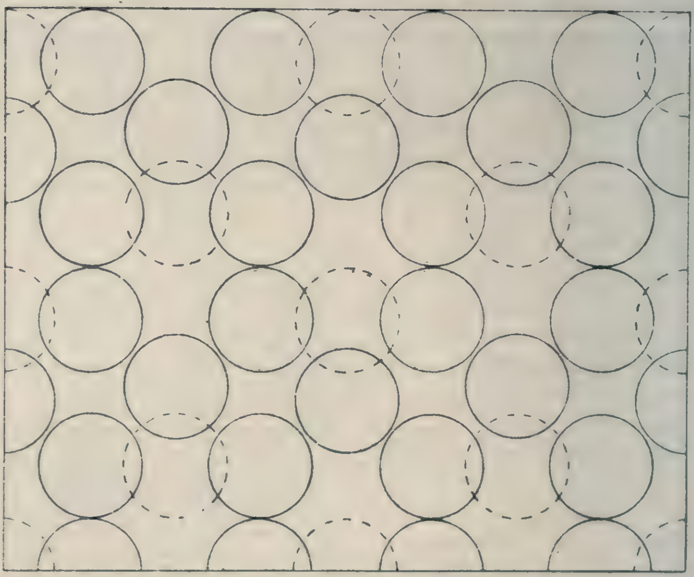
The unaltered marshalling of the large spheres in each molecular group which is thus prescribed, and the advancement of large spheres to occupy cavities left vacant by the removal of the small ones, is fittingly represented by the transition from the graphic formula of trimethylmethane to that of methyltrimethylene immediately accomplished by removing a hydrogen atom from each of two neighbouring branches of the molecule of the former, and restoring the linkage equilibrium by adding a link between the carbon atoms concerned, thus:



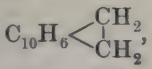
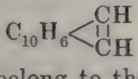
$$\begin{matrix}\mathrm{H}\\ \mathrm{CH_3}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix} \quad \text{to} \quad \begin{matrix}\mathrm{H}\\ \mathrm{CH_3}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{CH_2}\\ |\\ \mathrm{CH_2}\end{matrix}.$$

In connexion with the two methods just described for deriving an assemblage representing methyltrimethylene, it is suggested that the course followed involves the initial formation and the subsequent preservation of an approximately regular tetrahedral disposition of the contacts of the carbon spheres with other spheres of the same molecular unit; the functional identity of the molecular units here indicated will necessitate that the two assemblages should be regarded as an example of polymorphism.

FIG. 45.



The arguments stated and the data given in the previous pages indicate that an ethenoid compound is derived from the corresponding paraffinoid compound by the removal of the requisite proportion of hydrogen spheres from the assemblage, and the subsequent contraction necessary to restore close-packing to the assemblage. It would consequently be anticipated that pairs of substances of complex molecular constitution, the members of which differ in that a paraffinoid element, $\cdot CH_2 \cdot CH_2 \cdot$, in the one is substituted by an ethenoid element, $\cdot CH\!:\!CH\cdot$, in the other, might afford frequent instances of intimate crystallographic relationship; in such cases, the substitution just mentioned should occur in such a manner that the closing up of the assemblage would be manifested by a contraction in the direction of one of the properly selected equivalence parameters. Examples of this kind are not uncommon, and one may be here quoted.

Acenaphthene,  $C_{10}H_6\!<\!\begin{array}{l}CH_2\\ |\\ CH_2\end{array}$, is morphotropically related to acenaphthylene,  $C_{10}H_6\!<\!\begin{array}{l}CH\\ \|\\ CH\end{array}$ (Billows, *Zeitsch. Kryst. Min.*, 1903, **37**, 396); both belong to the orthorhombic system, and the axial ratios are respectively:

Acenaphthene, $a : b : c = 0·5903 : 1 : 0·5161$.
Acenaphthylene, $a : b : c = 0·5926 : 1 : 0·4996$.

The equivalence parameters corresponding with these axial ratios are:

Acenaphthene, $x : y : z = 3·3959 : 5·7527 : 2·9689$. $W = 58$
Acenaphthylene, $x : y : z = 3·4017 : 5·7404 : 2·8678$. $W = 56$.
Differences $-0·0058 + 0·0123 + 0·1011$.

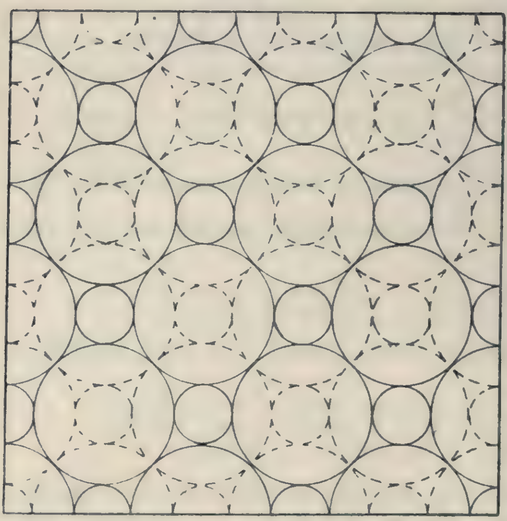
It is observable that the differences between corresponding equivalence parameters for the two substances are negligibly small in the directions x and y, but appreciably large in the direction of z; in this case the replacement of the paraffinoid by the ethenoid structural element has involved a closing up of the crystalline assemblage, which is only experimentally appreciable in the direction of the c or z axis. An equally striking example is afforded by the morphotropic relationship observed between dibenzyl and stilbene, which is referred to later (p. 2379).

The Acetylene Series, C_nH_{2n-2}.

The space formation of spheres, which corresponds with the characteristic acetylene grouping, $\cdot C\vdots C\cdot$, is rather more difficult to trace than that representing the double linking present in ethylene, but owing to the extreme simplicity of the molecular composition of the first member of the acetylene series, the possibilities to be submitted to consideration are so limited in number that examination of the arrangement to be described, which fulfils some of the principal conditions requisite, leaves practically no doubt that it is the one sought.

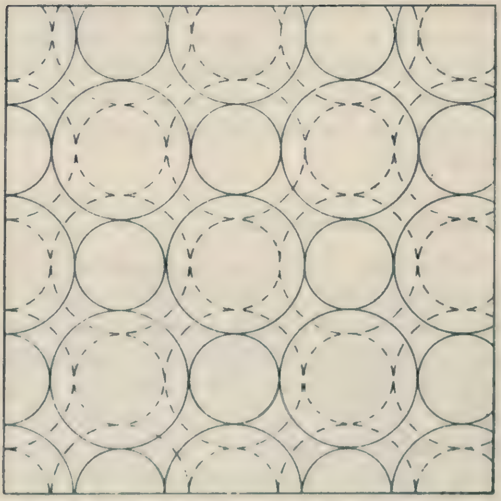
The assemblage representing acetylene itself is derived from a closest-packed cubic assemblage of spheres, each of the volume 4 (Fig. 1), in the following manner. Each of the large cavities in the assemblage, which are found at the centres of groups of six spheres and are just as numerous as the spheres, is occupied by a smaller sphere of such magnitude as just to touch the six spheres enclosing the cavity; the assemblage represented in Fig. 46 is the result. The smaller spheres which can thus be inserted are of a magnitude less than corresponds with the valency volume 1, and are next to be expanded until they attain this volume.

FIG. 46.



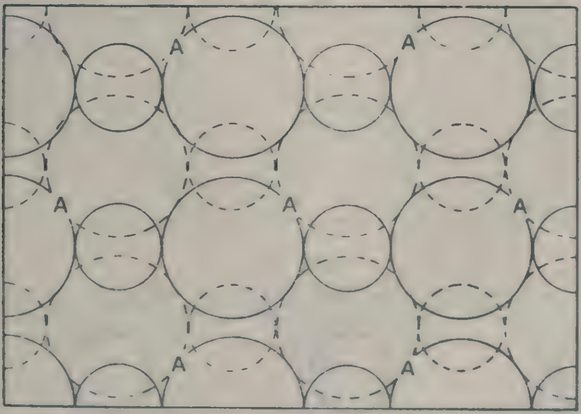
If the relative arrangement of the centres of both kinds remained unchanged during the expansion, it is evident that all the contacts between the larger spheres would be broken, as shown in Fig. 47, but it is possible for the large spheres to preserve some of their contacts, notwithstanding the presence of the smaller spheres, if slight mutual adjustment occurs. The assemblage can be regarded as composed of layers the planes of which are parallel to a plane drawn through opposite edges of a cube of the fundamental space-lattice; such a layer, viewed prior to the adjustment, is represented diagrammatically by the continuous lines in Fig. 48. Let therefore each larger sphere continue in closest contact with one other sphere of its own size, and let the partners be so selected that the contacts

FIG. 47.



of sphere with sphere are distributed through space as evenly as possible. The latter condition is fulfilled if the points of contact are approximately at the centres and angles of a cubic partitioning of space such that the length of a cube edge equals the translation of the assemblage along the directions in which carbon and hydrogen spheres are found placed alternately in contact. The assemblage thus modified consists of groups of a composition corresponding with acetylene, C_2H_2; the projections of the points at which the large spheres come into contact when the adjustment occurs are marked A in the diagram. The geometrical properties of the adjusted assemblage thus constituted parallel the chemical behaviour of acetylene, as will be perceived below in connexion with the homologues of the hydrocarbon. Owing to the fact that no crystallographic data are available for directly checking the geometrical results, the exact nature of the processes by which the succeeding terms of the acetylene series are arrived at, and the precise forms of the assemblages, are difficult to determine; the following is put forward, however, as the probable mode of deriving the correct form of assemblage for methylacetylene (allylene), $CH_3\cdot C⋮CH$.

FIG. 48.



Methylacetylene (Allylene).

From one of the two similar faces of a layer of complexes such as is depicted in Fig. 48, the small spheres are removed, so that the residue represents the radicle, $\cdot C⋮CH$; the stratum is then slightly distorted by diminishing its thickness and consequently increasing its face dimensions so as to make the latter equal to those of a layer of the unadjusted orthorhombic ethane assemblage, Fig. 49*b*. On the denuded face of a stratum of this kind, which is shown in Fig. 49*a*, is next grafted a stratum of methyl complexes (Fig. 49*b*), namely, a half stratum of the ethane assemblage (Fig. 23); the process is represented diagrammatically by superposing Fig. 49*b* on Fig. 49*a*. The composition of the resulting compound stratum

FIG. 49*a*.

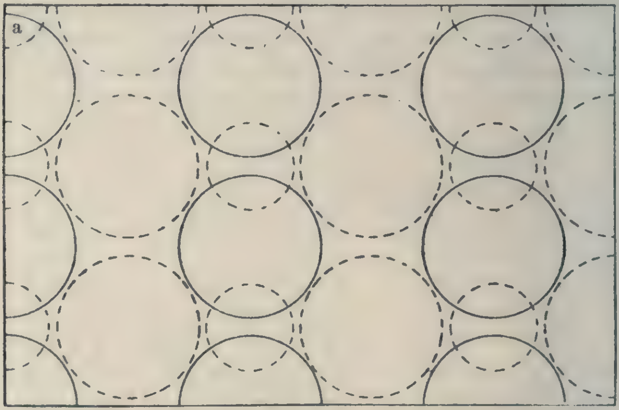
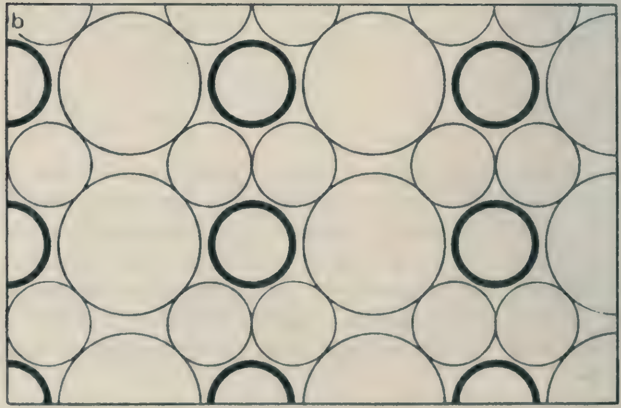


FIG. 49*b*.



is represented by the formula $CH_3 \cdot C \vdots CH$, and the corresponding equilibrium assemblage will consist of a number of such strata keyed into one another; succeeding strata will be oppositely orientated, and the contacts between them will consequently be of two different kinds occurring alternately. One kind will resemble the terminal contacts found in the acetylene assemblage, as above presented, and the other, those found in the normal paraffin assemblage of the orthorhombic form. As in most of the preceding cases, the marshalling described is represented in a simple form, and the assemblage must therefore be conceived to be subjected to such adjustment as is requisite to produce closest-packing of this marshalling. It is important to observe that the assemblage just

FIG. 50*a*.

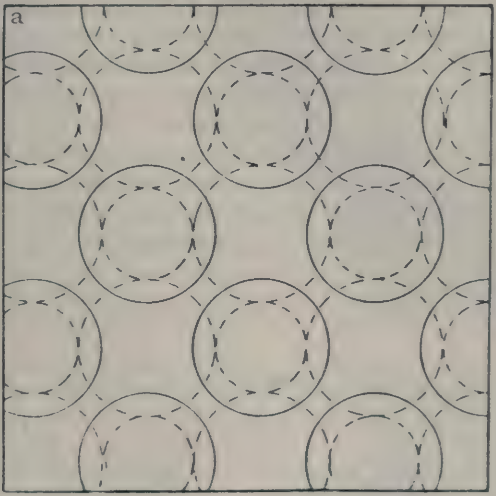
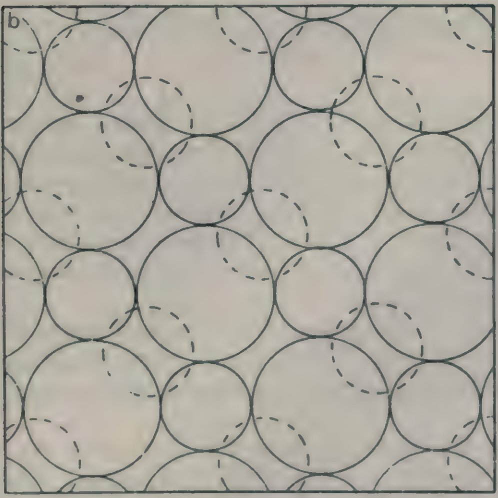


FIG. 50*b*.



described can be distorted so as to assume a tetragonal form without any considerable alteration of the environment of the constituent atoms; perhaps the simplest way of describing the result is to build up an assemblage from two kinds of tetragonal strata representing respectively the acetylenic remnant, $\cdot C \vdots CH$, and the methyl radicle, $\cdot CH_3$. The former is obtained from a tetragonal acetylenic layer (Fig. 47) by removing the hydrogen spheres from one of its faces, as shown by Fig. 50*a*, whilst the layer representing methyl is derived from the tetragonal ethane assemblage (Figs. 29 and 30), and its projection is represented diagrammatically in Fig. 50*b*. It is remarkable that in putting the two layers together the terminal face of the ethane stratum has in this case to be turned towards the denuded acetylene face, so that what was the inner face is now outwards; this is represented by superposing *b* on *a* of Fig. 50. The methylacetylene strata, $CH_3\cdot C\vdots CH$, as before, present opposite orientations in succeeding layers; in the tetragonal assemblage now being described, junctions, such as occur in acetylene, alternate with junctions having much the same marshalling as those of tetramethylmethane strata (p. 2348). The diagrams merely indicate the marshalling, and must be supposed subjected to adjustment which renders the packing closer.

FIG. 51.

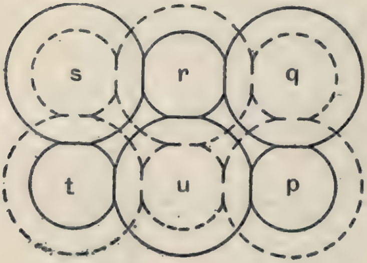
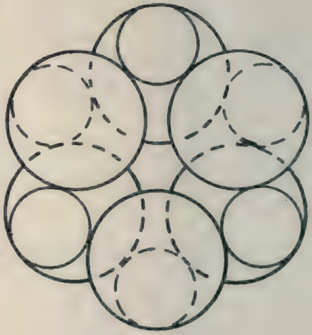


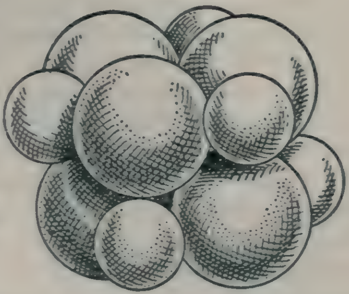
FIG. 52.



The assemblage representing the next homologue of the series, ethylacetylene, $CH_3\cdot CH_2\cdot C\vdots CH$, results from employing a butane stratum instead of an ethane one in the geometrical process described above.

It has been shown in the foregoing pages that the geometrical method indicates that the conversion of a paraffin assemblage into that of the corresponding olefinic and acetylenic hydrocarbon occurs by the excision of layers of hydrogen spheres, appropriately selected, in such a manner that the dimensions of the residual paraffinoid radicle suffer but little change. The paraffinoid, olefinic, or acetylenic assemblage can, in fact, be regarded as consisting of a paraffinoid assemblage into which have been appropriately intercalated layers of the composition $\cdot CH_2\cdot CH_2\cdot$, $\cdot CH{:}CH\cdot$, or $\cdot C\vdots C\cdot$ respectively, these layers being dimensionally compatible with the paraffinoid part of the assemblage. In this dimensional compatibility between the three elements of constitution just mentioned is found a complete explanation of the frequent occurrence of close morphotropic relationships between corresponding paraffinoid, olefinic, and acetylenic compounds, and for which no cause has hitherto been traced. For the present it will suffice to quote the axial ratios for the monosymmetric dibenzyl, stilbene, and tolane as illustrating the relationship referred to (Boeris, *Zeitsch. Kryst. Min.*, 1901, **34**, 298):

FIG. 53.



	$a : b : c.$	$\beta.$
Dibenzyl, $Ph\cdot CH_2\cdot CH_2\cdot Ph$ …………	2·0806 : 1 : 1·2522	115° 54′
Stilbene, $Ph\cdot CH{:}CH\cdot Ph$ … …………	2·1701 : 1 : 1·4003	114 6
Tolane, $Ph\cdot C\vdots C\cdot Ph$ …… ………………	2·2108 : 1 : 1·3549	115 1

The Conversion of Acetylene Derivatives into Aromatic Hydrocarbons.

The assemblages just put forward as representing acetylene and its homologues have been constructed in accordance with the principles of close-packing applied in numerous other cases, the existence of this condition consisting in the large number of spheres in contact with, or close proximity to, each sphere. Although uncorroborated to any considerable extent by crystallographic evidence, the correctness of the representation is strongly supported by the fact that the tetragonal assemblages described immediately provide a mechanism which can be shown to illustrate the well-known conversion of acetylene derivatives into aromatic hydrocarbons.

The acetylene assemblage has been derived from the closest-packed assemblage of equal spheres of the valency volume 4 by forcing spheres of valency volume 1 into the interstices which occur at the centres of close octahedral groups of six spheres and are as numerous as the large spheres. Before the insertion of the smaller spheres, the assemblage can be regarded as composed of identical groups of six spheres, and similarly, after the insertion of the hydrogen spheres, as built up of the composite groups of twelve spheres, six large and six small, depicted in Fig. 51. The latter groups, however, can be readily distorted into groups of the benzene configuration shown in Fig. 52, which has been previously described (Trans., 1906, **89**, 1693), and is shown in rough perspective in Fig. 53; this is easily seen by comparing Figs. 51 and 52. The acetylene assemblage of Fig. 48 can, consequently, be regarded as built up of units of the composition C_2H_2, each representing an acetylene molecule, or as consisting of units of the composition C_6H_6, each of which represents a distorted benzene complex.

The choice between the two kinds of partitioning can be expressed by the number of large spheres in immediate contact; if these touch two by two, while the pairs are not in contact but are kept apart by the smaller spheres, the acetylene grouping is indicated, but if the larger spheres form groups, each containing six carbon spheres in ring contact, each sphere of a layer of three being attached to two spheres of the neighbouring layer of three, the benzene configuration is portrayed. It is conceivable that the simpler form of grouping may give closest-packing when the ratio of the sphere magnitudes lies within certain narrow limits, and that when these limits are exceeded in one of the two directions, the other form of grouping may be brought about; the polymorphous forms of assemblage for benzene previously described would then follow from further change of the conditions. The passage from one grouping to the other above indicated will thus occur at some critical condition of temperature or the like; it involves no re-marshalling but some slight adjustment of the relative positions of the two sizes of spheres. The slight adjustment which is thus requisite to the conversion of the acetylene assemblage into an aggregate of units having the benzene configuration is the geometrical analogue of the conversion of acetylene into benzene by heat.

The acetylene assemblage, in accordance with our previous results, must be regarded as practically identical in form and relative dimensions with the assemblages of the halogen derivatives of the hydrocarbon; by replacing each hydrogen sphere in it by an iodine sphere of approximately the same valency volume, the assemblage representing the crystalline di-iodoacetylene would be obtained. Von Baeyer's observation (*Ber.*, 1885, **18**, 2269), that di-iodoacetylene, C_2I_2, is converted into hexaiodobenzene by slight warming or the action of light, is in complete accordance with this.

A similar kind of mechanism elucidates the polymerisation which occurs when monoiodo- or monobromo-acetylene is preserved in the crystalline or dissolved state, and which leads to the production of the 1 : 3 : 5-tri-iodo- or tribromo-benzene respectively (von Baeyer, *loc. cit.*). For the representation of these changes, the hydrogen spheres on one side only of the stratum of acetylene complexes are replaced by iodine or bromine spheres of approximately the same valency volume as hydrogen; the distortion of the assemblage for monoiodo- or bromo-acetylene thus obtained leads to the re-partitioning in the sense of the equation:

$$3CH{:}CI = C_6H_3I_3\ (1:3:5).$$

The compound tetragonal assemblage for allylene, $CH_3{\cdot}C{:}CH$, depicted in Fig. 49, was obtained by the intercalation of two kinds of strata, those, namely, of the acetylene and methane radicles. Polymerisation strictly corresponding with that observed is brought about geometrically by altering the acetylene stratum just as in the previous case; the three carbon spheres of a newly constituted benzene complex thus formed, which lie in one of the two planes, become respectively attached to three methyl groups of the adjoining stratum so as to give the symmetrical constitution of mesitylene.

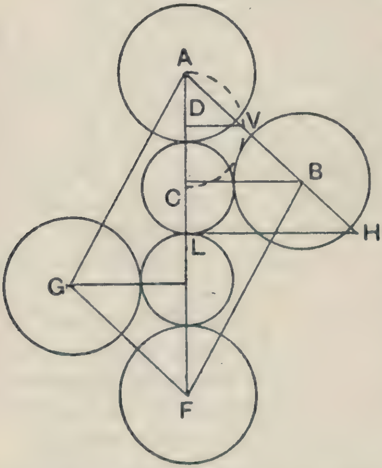
In the derivation of the assemblage for allylene, the hydrogen spheres on one side only of the acetylene layers were replaced by a layer of methyl complexes; if the hydrogen spheres on both sides of each acetylene layer are replaced by layers of methyl complexes, the assemblage produced represents that of the symmetrical dimethylacetylene (crotonylene), $CH_3{\cdot}C{:}C{\cdot}CH_3$. The passage by slight distortion of the acetylene layers to the benzene configuration involves the conversion of each set of three dimethylacetylene complexes into one molecular complex of hexamethylbenzene in a manner precisely paralleled by the observed facts.

If oxygen spheres are introduced into the allylene assemblage described above in the proportion of one for each acetylene unit present, and two hydrogen spheres are simultaneously introduced for each oxygen sphere, in accordance with the second geometrical property, an assemblage is obtained which has a constitution corresponding with that of acetone, $CH_3{\cdot}CO{\cdot}CH_3$. The removal of the elements of water from this assemblage, so as to convert it into the allylene assemblage, accompanied by the slight distortion which causes the assemblage to pass to the benzene form, corresponds geometrically with the observed conversion of acetone into mesitylene by the dehydrating action of sulphuric acid. The following method may be applied to the production of an assemblage for acetone, in which the process referred to can be readily traced.

The general methylene assemblage described above (p. 2326) can be distorted to an acute rhombohedral form without sensibly affecting the closeness of the packing; the volume of each rhombohedral unit cell, like that of the orthorhombic cell before described, is that proper for one radicle unit, CH_2. The corners of the cell are occupied by the centres of carbon spheres, and the cell contains at its centre a pair of hydrogen spheres, the pairs being similarly orientated. The resulting assemblage can be traced in the following simple manner. The assemblage may be regarded as consisting of similar layers of the same composition as the layers depicted in Fig. 19, the planes of centres being parallel to a plane drawn through the axis of a cell to contain one of the rhombohedral edges which intersect this axis; a constituent layer can be derived if the configuration of a single unit cell is ascertained in the following manner.

Two circles, centred at A and C, of which the diameters are in the ratios of those of the carbon and hydrogen spheres, are drawn in contact (Fig. 54); on the line joining the centres, AC, a semicircle, AVC, is erected, and AC is produced to cut the smaller circle in L. The line LH is drawn perpendicular to AL, AL is trisected in D, and DV is drawn perpendicular to AL to intersect the semicircle in V, A and V are joined, and the join produced to cut LH in H; VH is then bisected in B, and with B as centre a circle equal to circle A is drawn.

FIG. 54.



Since AD=1/3 AL, AV=1/3 AH=VB; therefore, since AVC is a right angle, AC=CB, and circle C, which touches circle A, also touches circle B. L is now used as a centre of symmetry, about which points, lines, and circles are symmetrically repeated, as shown in the figure; the parallelogram ABFG is the section of a rhombohedron of the form required, and the circles centred at A, B, F, and G are the sections of carbon spheres of which the centres lie at those angular points of the rhombohedron which are intersected by the plane of the section depicted; the small circles indicated are the sections of hydrogen spheres enclosed, each having contact with the other and with three carbon spheres lying on one side of L in a plane perpendicular to AL as well as with one carbon sphere of which the centre lies on this line. For, if the line ALF be made a trigonal axis, and by successive rotation through 120° about it, four other points are located from the points B and G, while points A and F remain unmoved, the eight points thus

FIG. 55.

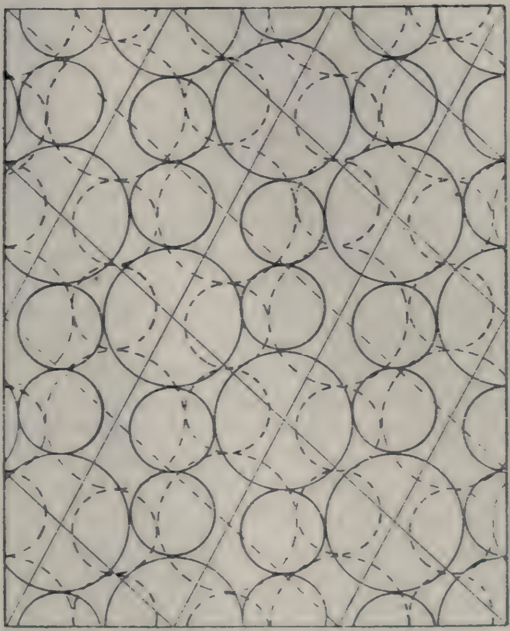


FIG. 56*a*.

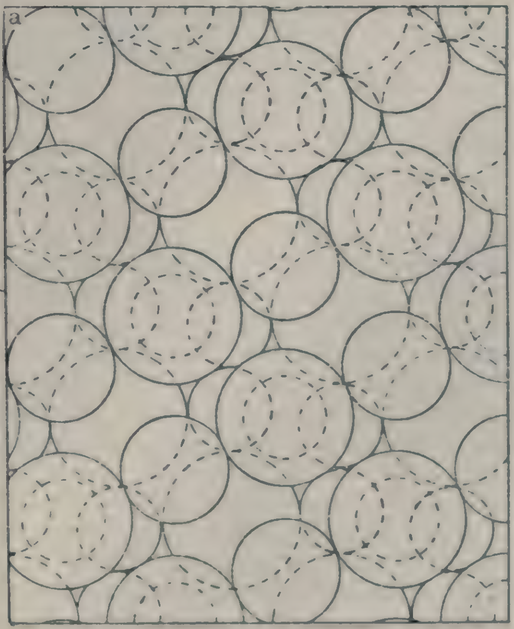


FIG. 56*b*.

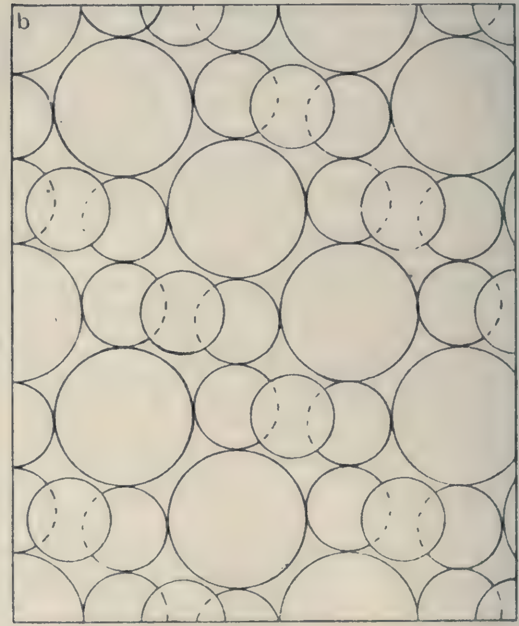
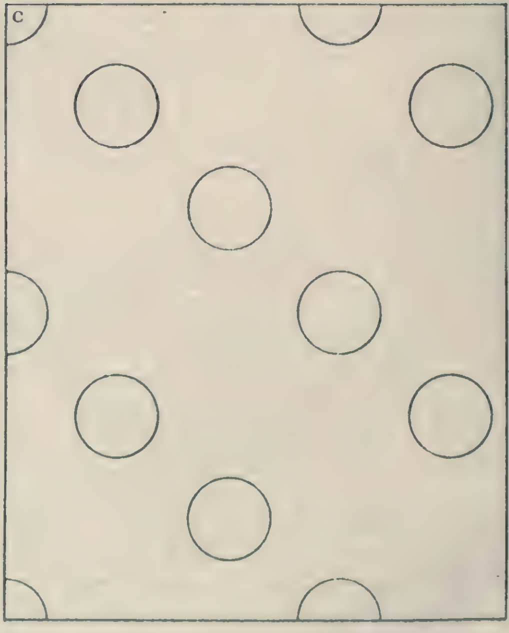


FIG. 56*c*



indicated are connected by the property that the six points not on the axis are equidistant from it and lie three and three on two planes which trisect the axis AF, a property characteristic of the angular points of a rhombohedron. The proof of the existence of this property lies in the fact that the traces of the planes referred to, being the horizontal lines through B and G, respectively trisect the semi-axes AL and FL.

When space has been partitioned by means of three sets of parallel equidistant planes into rhombohedra of the form indicated, and carbon spheres have been placed with centres at all the angles, while pairs of hydrogen spheres occupy the cell centres, each large sphere is in contact with eight small spheres and almost in contact with six large spheres, while each small sphere touches four large spheres and one small one. This kind of arrangement can be traced in Fig. 55, which shows layers constructed according to the cell conditions derived above; the continuous and discontinuous lines respectively depict projections of succeeding layers.

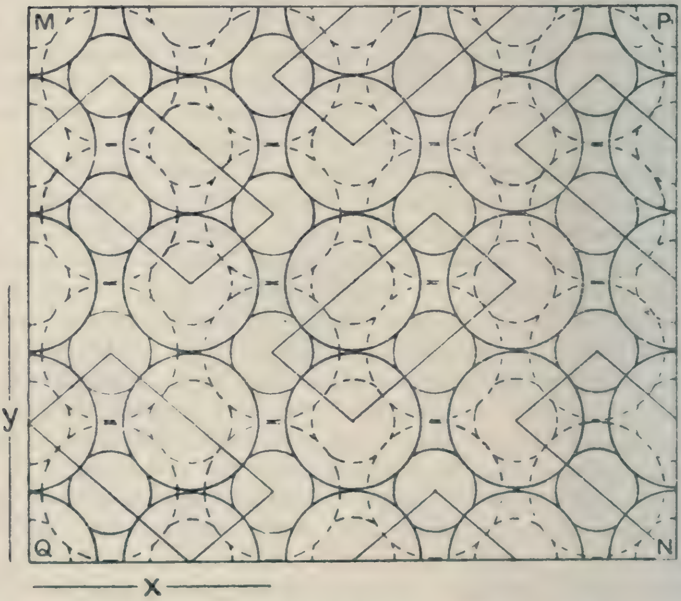
In order to derive from the methylene assemblage of the form thus described an assemblage for acetone, $CH_3 \cdot CO \cdot CH_3$, three succeeding layers are taken, and an oxygen sphere substituted for each pair of hydrogen spheres of the central layer of the three; this can be done without any sensible change in the form of the rhombohedral cell. A number of sets of three layers thus modified must then have hydrogen spheres added, just as in the case of the previously described methylene assemblage, so as to produce strata which appropriately represent the formula of acetone; the resulting assemblage in its most symmetrical condition is indicated by superposing *b* on *a* of Fig. 56, *a* representing the two layers, CH_2 and CO respectively, with the terminal hydrogen spheres added, and *b* representing a single layer, CH_2, with its terminal hydrogen spheres.

Geometrical complexes of the composition OH_2 can be readily recognised in the assemblage described, each oxygen sphere being nearly in contact with four hydrogen spheres, two above and two below the plane of the layer. The withdrawal of the pairs of hydrogen spheres of one of the layers simultaneously with the oxygen spheres of the next layer, with which they are nearly in contact, deprives the middle carbon layer of all its smaller spheres, and leaves but one hydrogen sphere, namely, the end one, to be allotted to each of the carbon spheres of an end layer; this, when the assemblage is closed up after the extraction of the OH_2 complexes, leads to the marshalling above deduced for allylene, $CH_3 \cdot C \vdots CH$, and subsequently the deformation already referred to converts the allylene assemblage into that proper for mesitylene (p. 2381).

A mechanism similar in kind to that explained and illustrated above is apparently applicable to the more complex cases presented by the various pyridine, quinoline, and quinaldine syntheses.

The geometrical simplicity of the operation by which the elements of water can be introduced into an acetylenic assemblage is completely paralleled by the ease with which acetylene, CH⋮CH, reacts with water under the influence of a catalyst to yield acetaldehyde, $CH_3{\cdot}CHO$. In order to represent the assemblage corresponding with the latter substance, two of the layers of a methylene assemblage of rhombohedral form, as just described, are requisite, the pairs of hydrogen spheres in one of the two layers being exchanged for single oxygen spheres. The appropriate addition of hydrogen spheres at the opposite faces completes a stratum corresponding with the constitution of acetaldehyde; the latter is represented by superposing *c* on *a* of Fig. 56.

FIG. 57.



In connexion with the distorted configuration (Fig. 51) just described as an intermediate form displayed by the benzene complex during its production from acetylene, it is significant that units having this configuration can be fitted together to make an assemblage which is compatible with the axial ratios and crystalline form of benzene itself, but which is not identical with the benzene assemblage previously described (Trans., 1906, **89**, 1694, Fig. 3). The somewhat remarkable fact that the same spheres present in the same proportions are capable of two widely different arrangements presenting almost the same crystalline form and axial ratios is traceable to the spheres occurring in continuous strings in two of the three axial directions; thus, in the earlier assemblage just referred to, the large spheres range in contact in the direction of the axis y, and large and small spheres alternately range in contact along the direction of the axis z. The dimensions y and z closely correspond, in fact, with twice the diameter of a carbon sphere and to the sum of the diameters of a carbon and a hydrogen sphere respectively; any assemblage in which carbon and hydrogen spheres range in this manner along directions of translations will consequently be morphotropically related to the benzene assemblage previously described. The assemblage of the distorted units of Fig. 51 is shown diagrammatically in Fig. 57, in which each of the parallelograms indicated marks the projection of the centre portion of a column of benzene complexes of which the axis is perpendicular to the plane of the figure; the sphere centres of each single molecular unit are projected on the outline of some one such parallelogram. The partitioning of this diagrammatic assemblage into molecular complexes can occur in several different ways, which produce identical results; the parallelograms are drawn appropriately for two of these ways, the column indicated by a single parallelogram being divisible into molecular units in two ways (compare Trans., 1906, **89**, 1696). The values of x and y used in the construction of Fig. 57 are those calculated for crystalline benzene, in which

$$x : y : z = 3{\cdot}101 : 3{\cdot}480 : 2{\cdot}780.$$

The assemblage shown in Fig. 57, being unadjusted, is equally applicable to acetylene and benzene; it shows neither of the kinds of coalition of spheres to form a complex which have respectively been described as productive of molecular units proper to these compounds. This accounts for the marked flattening of the spheres which is found to be necessary in order that they may be packed into the space accorded by the benzene valency volume of $W = 30$. In three directions in the assemblage, namely, one perpendicular to the plane of the diagram, and two, those of the diagonals MN, PQ, the large and small spheres alternate. In the diagram they are represented as precisely in line, but this will not be strictly the case, especially along the directions of the diagonals; increased closeness of packing, and therefore less flattening, will result from a slight zigzagging of the positions of the two sets of centres of the same string.

The conclusion referred to, that continuous strings of spheres are present in which the two sizes alternate, throws light on the numerous cases in which the value of the z axis for benzene is very approximately presented as one of the equivalence parameters of benzene derivatives; many such instances have been recorded by Jerusalem (Trans., 1909, **95**, 1275) and by Armstrong (this vol., p. 1578).

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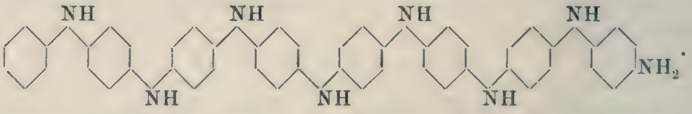
CCXLIII.—*Aniline-black and Allied Compounds. Part I.*

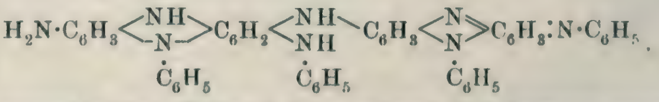
By ARTHUR GEORGE GREEN and ARTHUR EDMUND WOODHEAD.

ALTHOUGH the recent researches of Willstätter and his pupils (Willstätter and Moore, *Ber.*, 1907, **40**, 2665; *J. Soc. Dyers*, 1908, **24**, 4; Willstätter and Dorogi, *Ber.*, 1909, **42**, 2147, 4118) have added much of value to our knowledge of the complex oxidation products of aniline, the constitution of aniline-black and of its intermediate products still cannot be regarded as completely elucidated. The view advanced by Willstätter, that these compounds are all to be regarded as indamine-like derivatives of the eight-nucleal chain compound (leucoemeraldine):



will scarcely gain acceptance without further evidence. As Bucherer has pointed out, it might a priori be expected that substances of such a type would exhibit a high degree of instability, and would readily decompose into simpler compounds under the influence of acids, etc.

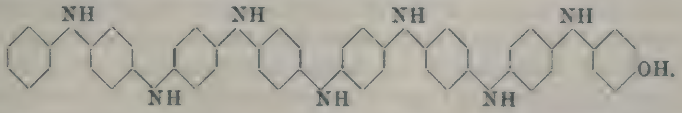
Amongst other arguments in support of the chain structure, Willstätter has shown that the quantitative conversion into p-benzoquinone is only compatible with the existence of di-para-connexions, and is entirely opposed to an azine structure, such as that suggested by Bucherer (*Ber.*, 1909, **42**, 2931):



$$H_2N\cdot C_6H_3<\begin{matrix}NH\\ -N-\\ \dot{C}_6H_5\end{matrix}>C_6H_2<\begin{matrix}NH\\ NH\\ \dot{C}_6H_5\end{matrix}\diagdown C_6H_3<\begin{matrix}N\\ N\\ \dot{C}_6H_5\end{matrix}>C_6H_3{:}N\cdot C_6H_5.$$

In respect to the validity of this argument, it is, however, necessary to point out that a sharp distinction must be made between the primary oxidation products of aniline (emeraldine, nigraniline, etc.) and the condensation products of these with aniline ("ungreenable aniline-black"), which latter alone can be properly regarded as true aniline-black. Willstätter's experiments refer only to the former class of compounds, and it yet remains to be shown what yield of *p*-benzoquinone is obtainable from the latter. It is quite conceivable, and in fact probable, that whilst the former possess a di-para chain or ring structure, the "ungreenable aniline-black," that is, true aniline-black, is an azine (Green, *The Chemical Technology of Aniline-black*, 7th Internat. Congress of Applied Chemistry, London, 1909; *J. Soc. Dyers*, 1909, **25**, 188). Only the "ungreenable aniline-black" can be correctly regarded as a highly stable compound; the primary oxidation products probably owe much of their apparent stability to their insolubility in water and aqueous solvents, for when dissolved in pyridine, etc., they exhibit a much greater tendency to undergo change.

The view held by Willstätter that "ungreenable aniline-black" is a compound of the same type as the primary oxidation products (that is, contains an eight-nucleal chain, and only differs from the primary products in the degree of oxidation and the replacement of the terminal NH by O), is opposed, in our opinion, to the experimental facts. Were this view correct, the behaviour with sulphurous acid of the two oxidation stages he describes should be the same, that is to say, both compounds should be reduced to the green monoquinonoid stage, and by the application of a stronger reducing agent all should be reduced to the mother substance, that is, to the oxygen analogues of leucoemeraldine:



Furthermore, this reduction-product, like leucoemeraldine itself, would certainly be a tolerably stable substance, giving, on air oxidation, only the lowest quinonoid stage, and requiring the application of a strong oxidising agent to reconvert it into the original tri- or tetra-quinonoid compound. These properties are not exhibited either by the preparations described by Willstätter as "hydrolysed triquinonoid and tetraquinonoid blacks," or by the "ungreenable aniline-black" produced on the fibre. The latter is not reduced at all by sulphurous acid, and by stronger reducing agents, such as hyposulphites, it is converted into a leuco-compound which is rapidly re-oxidised by air to the original "black," and that apparently without passing through any lower stage of oxidation. Moreover, the facts known respecting the conditions of formation of "ungreenable aniline-black" clearly show that it cannot be a product of further oxidation alone, but is a condensation product with aniline of a different type to the simpler oxidation products from which it is formed (Green, *loc. cit.*).

In order to throw more light on this complicated subject, it has appeared to us necessary to obtain, in the first instance, further evidence for the molecular weight and constitution of the primary oxidation products (emeraldine and nigraniline), and we have attempted to do this by determining, on the one hand, the quantity of hydrogen required to reduce these products to leucoemeraldine, and, on the other, the quantity of oxygen necessary to oxidise each stage into the next. The data obtained in this manner, combined with the fact that we have been able to recognise four distinct stages of oxidation of leucoemeraldine, support Willstätter's view of an eight-nucleal molecule, but do not agree with the constitution assigned by Willstätter and Dorogi to the compounds they prepared.

Assuming the correctness of the eight-nucleal structure for the primary oxidation products, it still remains an undecided question whether the aniline residues are to be regarded as united in an open or in a closed chain, but without attempting to decide this point we shall make use of the open-chain formulæ to express provisionally the analytical results. The constitution of "ungreenable aniline-black" we reserve for discussion in a later communication.

Before proceeding to a consideration of the results obtained, it is desirable to attempt to clear up some of the existing confusion regarding the various oxidation products of aniline and their nomenclature. Much of the obscurity in this subject arises from the fact that no criterion of purity has hitherto existed, and that the products obtained have been doubtless largely mixtures. Unsuitable nomenclature has still further added to the confusion. Thus the name "emeraldine," which properly belongs to the first acid-oxidation product of aniline—a violet-blue base giving green salts, and well known to dyers of aniline-black—has been transferred by Willstätter and Moore to an entirely different compound, namely, the blue imide obtained by polymerisation of phenylquinonedi-imide, which was apparently first mistaken for emeraldine by Caro. On the other hand, for the true emeraldine, originally so-called by Crace-Calvert and Lowe, the name "triquinonoid aniline-black" is now proposed by Willstätter and Dorogi, although emeraldine is neither black nor (as will be shown later) is it triquinonoid. In justification for this confusing and unnecessary transfer of names, Willstätter and Dorogi advance the incomprehensible plea that "technisches Emeraldine längst nicht mehr existirt."

The various oxidation products which have been described under the name of aniline-black by the earlier authors (Müller, Nietzki, Kayser, Guyard, etc.) are lacking in any criterion of purity or individuality beyond that furnished by elementary analysis, which in this case is quite inconclusive and valueless. The discovery that the primary oxidation products (emeraldine and nigraniline bases) are readily soluble in somewhat diluted organic acids, such as 80 per cent. acetic acid and 60 per cent. formic acid (the former base giving a green solution, and the latter a blue), whilst the higher condensation products are insoluble in these solvents, has provided us with a valuable means for diagnosis and separation, by means of which we have been able to show that all the above-mentioned so-called "aniline-blacks" consist mainly of emeraldine and nigraniline mixed with varying proportions of higher condensation products. These "blacks" prepared in substance therefore do not properly correspond with the aniline-black produced on the fibre, since in the latter case the higher condensation products are either exclusively present (ungreenable blacks) or largely predominate (greenable blacks).

In order to simplify the nomenclature, we propose that the term "aniline-black" should be restricted to the higher condensation products (ungreenable black), whilst the original names "emeraldine" and "nigraniline" should be retained for the primary oxidation products. As, however, there is a stage of oxidation below emeraldine and one above nigraniline, we propose for these the names "protoemeraldine" and "pernigraniline." All four substances, protoemeraldine, emeraldine, nigraniline, and pernigraniline, are quinonoid derivatives of the same parent substance, to which we have given the name "leucoemeraldine." Into this compound they are all converted on reduction, and from it they can all be produced by oxidation. At present the protoemeraldine stage has only been obtained in the *o*-toluidine series, whilst pernigraniline is too unstable to isolate in a dry state.

Emeraldine.

This compound is the first clearly defined stage in the oxidation of aniline in an acid medium, whatever the oxidising agent employed. When a chlorate is used, the reaction tends in part to at once proceed further with production of more or less nigraniline, but with hydrogen peroxide, if not used in excess, the oxidation stops at the emeraldine stage. If the reaction is effected in the cold and in the presence of an excess of acid, emeraldine and nigraniline are nearly the sole products, but if the mixture is neutral or only slightly acid, a certain quantity of condensation products (ungreenable black) is also produced. An excess of acid is therefore a necessary condition for preparing emeraldine in a pure state. As the result of a series of experiments, proportions corresponding with 1 mol. of aniline hydrochloride to 1·33 mols. of oxygen and 1 mol. of hydrochloric acid were found the most suitable.

Emeraldine is also produced by the further oxidation of the blue imide, $C_6H_5\cdot NH\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot N\colon C_6H_4\colon NH$, of Willstätter and Moore (termed "emeraldine" by these authors).

I. A solution of 100 grams of aniline hydrochloride, 42 grams of sodium chlorate, and 46·5 c.c. of hydrochloric acid (33 per cent. HCl) in 1800 c.c. of water, to which 2 drops of syrupy vanadium chloride are added, is kept in the cold for from two to three days. The precipitate is then collected, washed thoroughly with water, basified by mixing the paste with dilute ammonia in a mortar, finally washed with alcohol and with water, and dried at 35—40°. The product thus obtained contains a varying amount of nigraniline, which may be readily converted into emeraldine by warming the precipitate with dilute hydrochloric acid before basifying. Pure emeraldine may also be obtained by dissolving the crude base in 50 parts of 80 per cent. acetic acid, filtering from any insoluble matter, reprecipitating by addition of dilute hydrochloric acid, collecting the hydrochloride, and finally basifying the precipitate with ammonia. During this process the nigraniline present is converted into emeraldine.

II. A solution of 50 grams of aniline hydrochloride in 2½ litres of water, to which is added 135 c.c. of hydrochloric acid (33 per cent. HCl), 380 c.c. of hydrogen peroxide solution (4·6 per cent.), and 0·5 gram of ferrous sulphate, is kept in the cold for twenty-four hours. The precipitated emeraldine is collected, washed, and basified with ammonia.

III. Ten grams of *p*-aminodiphenylamine are dissolved together with 27 c.c. of hydrochloric acid (33 per cent. HCl) in 1 litre of water. After cooling to 0—5° by addition of ice, 78 c.c. of hydrogen peroxide (4·7 per cent.), followed by 0·1 gram ferrous sulphate, are added. The hydrogen peroxide used was rather more than twice the quantity required to convert the aminodiphenylamine into Willstätter and Moore's blue imide. On adding the iron salt, a voluminous indigo-blue precipitate of the imide was first produced, which, after about twelve to twenty-four hours, slowly lost its blue colour and became green, while the excess of peroxide disappeared and an odour of *p*-benzoquinone was apparent. The mixture was warmed on the water-bath, and the precipitate collected, washed, and basified with ammonia.

When prepared by either of these methods, the emeraldine base forms an indigo-blue powder, which, when purified by the acetic acid method, has a bronzy lustre. When dried at a low temperature it retains a remarkably large amount of water (about 30 per cent.). It is insoluble in alcohol, benzene, chloroform, etc., but dissolves readily in cold pyridine, giving a bright blue solution. This solution is, however, very unstable, for in a short time the greater part of the product separates out again as a colloidal precipitate. This precipitate consists of a condensation product of quite different properties to the original emeraldine. In concentrated sulphuric acid, emeraldine dissolves with a reddish-violet colour, and on addition of water a bright green precipitate of the sulphate is obtained. Towards acetic and formic acids the behaviour of emeraldine and nigraniline is very remarkable. These bases are insoluble in glacial acetic acid or in concentrated formic acid, and are also insoluble in these acids when fairly dilute, but in acids of medium concentration, that is, in acetic acid of about 80 per cent. or in formic acid of about 60 per cent., they dissolve readily. The solutions obtained with emeraldine are yellowish-green, and give a green precipitate on the addition of mineral acids or salts. By means of such a solution, the various stages of oxidation can be very effectively demonstrated, for on addition of a very dilute solution of chromic acid the green colour of the solution first changes to pure blue (nigraniline), and then, as more oxidising agent is added, to violet (pernigraniline), finally giving a violet precipitate (pernigraniline chromate). If to the violet solution of the pernigraniline a very weak solution of sodium hydrogen sulphite is added, these colour changes occur in the opposite direction, namely, from violet to blue, and from blue to green. Stronger reducing agents, such as phenylhydrazine, sodium hyposulphite, or titanium trichloride, convert emeraldine into leucoemeraldine.

In order to determine the quantity of hydrogen required for conversion of emeraldine into leucoemeraldine, the acetic acid solution was titrated with titanium trichloride according to Knecht's method, the analysis being carried out as follows. One gram of emeraldine in fine powder is weighed into a 250 c.c. flask containing 50 c.c. of water, and well shaken to prevent any of the powder agglomerating into lumps. Glacial acetic acid is then added until the flask is about three-quarters full, the contents well shaken, and heated on the water-bath for fifteen minutes to about 90° to ensure conversion of all nigraniline present into emeraldine. The solution is then cooled, and made up to the mark with glacial acetic acid. For each titration, 25 c.c. of this solution (= 0·1 gram of substance) are transferred, by means of a pipette, to a conical flask, and mixed with 25 c.c. of water and a measured excess of titanium trichloride, the strength of which is re-determined each day. The mixture is kept in the cold for ten to fifteen minutes, air being excluded by a slow stream of carbon dioxide. At the end of this time the solution is quickly filtered from the precipitated leucoemeraldine, employing a funnel and filter paper enclosed in a vessel filled with carbon dioxide. An aliquot portion of the whole (50 c.c.) is then transferred to another flask also containing carbon dioxide, and at once titrated with a standard ferric alum solution, employing ammonium thiocyanate as indicator. In calculating the results, the percentage of water, chlorine, and ash is allowed for, and a further small correction, determined by parallel blank experiments made under exactly the same conditions, is introduced for the loss of titanium trichloride oxidised by air during the operation. The first preparation analysed (obtained by method I) contained 31·9 per cent. of water, 1·1 per cent. of chlorine, and 0·1 per cent. of ash. The following results were obtained:

No. of experiment.	Vol. of $TiCl_3$ run in, c.c.	Vol. of $TiCl_3$ unoxidised, c.c.	Vol. of $TiCl_3$ oxidised by air, c.c.	Hydrogen value of 1 litre $TiCl_3$, gram.	Percentage of hydrogen on pure dry emeraldine.
1	25	13·70	1·77	0·0374	0·533
2	25	14·15	0·92	0·0366	0·543
3	25	14·15	0·92	0·0366	0·543
4	25	13·23	1·30	0·0358	0·560
5	25	13·65	1·34	0·0358	0·536
6	25	13·55	1·33	0·0358	0·542
7	25	13·47	1·29	0·0358	0·545
8	25	13·47	1·29	0·0358	0·545
				Mean.........	0·543

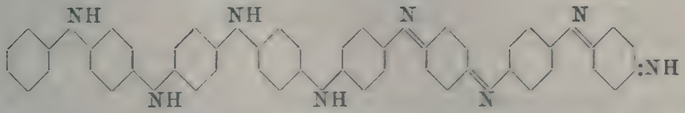
A second series of estimations was made with a larger excess of titanium trichloride and another preparation of emeraldine containing 30·65 per cent. of water, 1·0 per cent. of chlorine, and 0·1 per cent. of ash. Using 0·1 gram for each titration, the following results were obtained:

No. of experiment.	Vol. of $TiCl_3$ run in, c.c.	Vol. of $TiCl_3$ unoxidised, c.c.	Vol. of $TiCl_3$ oxidised by air, c.c.	Hydrogen value of 1 litre $TiCl_3$, gram.	Percentage of hydrogen on pure dry emeraldine.
1	50	40·69	0·87	0·0442	0·547
2	50	40·59	0·87	0·0442	0·553
3	50	40·80	0·88	0·0442	0·540
4	50	40·69	0·87	0·0442	0·547
				Mean.........	0·547

Figures of the same order were also obtained by direct titration of the acetic acid solution with titanium trichloride, although, owing to the uncertain end-point, the results were not as trustworthy as those obtained by the indirect method.

The mean value of the two series of determinations was 0·545 gram of hydrogen for 100 grams of pure dry emeraldine.

A diquinonoid compound of the formula:



would require 0·555 per cent. of hydrogen for complete reduction to the leuco-compound.

In order to estimate the quantity of oxygen consumed in the conversion of emeraldine into nigraniline, two methods have been adopted. The first consists in titrating an acetic acid solution of emeraldine with a standard solution of chromic acid until the pure blue colour of the nigraniline is reached. The second consists in separately titrating emeraldine and nigraniline until the violet pernigraniline chromate is completely precipitated. Deduction of the quantity of chromic acid required to reach this point for nigraniline from the quantity required to reach the same point for emeraldine gives the quantity consumed in oxidising emeraldine into nigraniline. Owing to the more definite end-point, the latter method is the more trustworthy.

I. Twenty-five c.c. of emeraldine solution, containing 0·1 gram of substance dissolved in 80 per cent. acetic acid, were diluted with 25 c.c. of water, and titrated with a solution of chromic acid containing 3·52 grams of chromium trioxide per litre (equal to 0·845 gram of oxygen per litre). The emeraldine employed contained 31·9 per cent. of water, 1·1 per cent. of chlorine, and 0·1 per cent. of ash and 1·5 c.c. of chromic acid (several experiments) were required to give a pure blue colour. Correcting for contents of water, chlorine, and ash, this is equivalent to a consumption of 1·9 grams of oxygen per 100 grams of pure dry emeraldine for oxidation to nigraniline.

II. (*a*) Twenty-five c.c. of emeraldine solution, containing 0·1 gram of substance dissolved in 80 per cent. acetic acid, were diluted with 25 c.c. of water, and titrated with a solution of chromic acid containing 0·704 gram of chromium trioxide per litre (equal to 0·169 gram of oxygen per litre) until the precipitation of the violet pernigraniline chromate was complete, and no further change of colour took place. The emeraldine employed contained 30·65 per cent. of water, 1 per cent. of chlorine, and 0·1 per cent. of ash.

No. of experiment.	Weight of emeraldine, gram.	Vol. of CrO_3 required, c.c.	Percentage of oxygen on pure dry emeraldine.
1	0·1	24·5	6·07
2	0·1	25·0	6·19
3	0·1	25·0	6·19
4	0·1	24·5	6·07
		Mean.........	6·13

(*b*) A weighed quantity of nigraniline (preparation see later) was added in a state of fine powder to 5 c.c. of water. The whole was cooled in ice, 20 c.c. of glacial acetic acid added, the mixture shaken until dissolved, and then at once titrated with chromic acid as above. The nigraniline employed contained 11·28 per cent. of water, 1·12 per cent. of chlorine, and 1·3 per cent. of ash:

No. of experiment.	Weight of nigraniline, gram.	Vol. of CrO_3 required, c.c.	Percentage of oxygen on pure dry nigraniline.
1	0·0950	19·5	4·02
2	0·0983	20·0	3·98
3	0·1257	25·0	3·89
4	0·1017	21·0	4·04
		Mean.........	3·98

Deducting 3·98 from 6·13 gives 2·15 as the percentage of oxygen required to oxidise pure dry emeraldine into nigraniline. If emeraldine has the above formula, it would require, theoretically, 2·20 per cent. of oxygen for the removal of two hydrogen atoms, that is, to introduce one quinonoid group.

Nigraniline.

The best method for the preparation of nigraniline in substance was found to be the oxidation of emeraldine base (or the mixture of emeraldine and nigraniline obtained by the chlorate oxidation), using an excess of hydrogen peroxide in an ammoniacal solution. For instance, the precipitate obtained by oxidising 40 grams of aniline hydrochloride and 18·6 c.c. of hydrochloric acid with 16·8 grams of sodium chlorate in presence of vanadium, as already described, is basified with ammonia, and the washed product, without being dried, is evenly suspended in 6 litres of water, to which 400 c.c. of hydrogen peroxide (3 per cent.) and 40 c.c. of concentrated ammonia are added. After keeping overnight, the precipitate is collected, washed well, and dried at 35°. The product contained 11·28 per cent. of water, 1·12 per cent. of chlorine, and 1·30 per cent. of ash.

Nigraniline base forms a bluish-black powder with a bronzy lustre. Like emeraldine, it is insoluble in most solvents, but dissolves in cold pyridine with a bright blue colour. The salts are blue, not dark green as stated in the literature. This error arises from the fact that nigraniline salts are very unstable, and both in substance and on the fibre are readily converted into salts of emeraldine. The change takes place slowly in the cold, but more rapidly on heating, and is accompanied by the production of *p*-benzoquinone. One part of the nigraniline is oxidised to *p*-benzoquinone, whilst another part is reduced to emeraldine, a fact which affords an explanation of the well-known "greening" of certain blacks on the fibre when exposed to an acid atmosphere. Similarly, when nigraniline is dissolved in concentrated sulphuric acid, it gives a violet solution of rather bluer shade than that of emeraldine, but on pouring into water, decomposition occurs, and a bright green precipitate of emeraldine sulphate is produced. Nigraniline dissolves readily and completely in cold 80 per cent. acetic acid or in 60 per cent. formic acid, giving pure deep blue solutions. These solutions, on warming, quickly change in colour to the green of the emeraldine salt. In contrast to the instability of the salts, nigraniline base is quite stable.

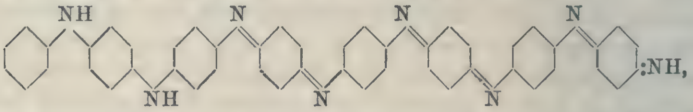
In performing the quantitative reduction of nigraniline, it is essential for the above reasons to avoid all heating in making the solution, and to effect the reduction as rapidly as possible. The operation is therefore carried out as follows. A weighed quantity of nigraniline (about 0·1 gram), which must be very finely powdered to ensure quick and complete solution, is suspended in 5 c.c. of water contained in a small flask. The flask is then cooled in ice for ten minutes, 20 c.c. of glacial acetic acid added, and the mixture shaken for half a minute, by which time the substance should have dissolved completely. Before the addition of the acetic acid, the air in the flask is expelled by carbon dioxide. The titanium trichloride solution is then added, and the titration effected in the same manner as with emeraldine:

No. of experiment.	Weight of nigraniline taken, gram.	Vol. of $TiCl_3$ run in (1 litre = 0·0307 gram of hydrogen), c.c.	Vol. of $TiCl_3$ left unoxidised, c.c.	Vol. of $TiCl_3$ oxidised by air, c.c.	Percentage of hydrogen on pure dry nigraniline.
1	0·1009	40	17·3	0·87	0·771
2	0·0673	40	23·85	1·20	0·791
3	0·1089	40	15·62	0·78	0·772
4	0·1320	50	20·47	0·63	0·781
5	0·1198	50	23·38	0·72	0·770
6	0·1108	50	24·35	0·75	0·801
				Mean.........	0·781

Another series of titrations made with a stronger titanium solution (1 litre = 0·0442 gram of hydrogen) gave the following results:

No. of experiment.	Weight of nigraniline taken, gram.	Vol. of $TiCl_3$ run in (1 litre = 0·0307 gram of hydrogen), c.c.	Vol. of $TiCl_3$ left unoxidised, c.c.	Vol. of $TiCl_3$ oxidised by air, c.c.	Percentage of hydrogen on pure dry nigraniline.
7	0·1386	50	27·98	0·51	0·797
8	0·0900	50	35·06	0·63	0·816
9	0·1090	50	32·10	0·58	0·816
10	0·1035	50	32·95	0·60	0·816
				Mean.........	0·811

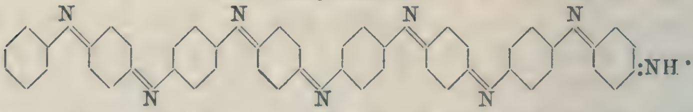
A triquinonoid compound of the formula:



would require 0·835 per cent. of hydrogen for complete reduction to leucoemeraldine. This formula is also supported by the oxidation numbers given under emeraldine.

Although the above formula is the same as that given by Willstätter and Dorogi to the preparation which they term "triquinonoid aniline-black," yet the compound described and analysed by them can scarcely be identical with nigraniline, for the properties do not correspond. If these authors originally had nigraniline in hand, it must have suffered conversion into emeraldine, and probably into further decomposition products by the process of purification employed.

Pernigraniline.



When a solution of emeraldine or nigraniline in acetic or formic acid is treated with an excess of a powerful oxidising agent, such as chromic acid or ammonium persulphate, the oxidation proceeds beyond the nigraniline stage, giving rise to a violet precipitate, which, on basifying with ammonia, yields a purple-brown compound, "pernigraniline." This substance is exceedingly unstable, decomposing slowly on drying, or even if kept in the paste form, with reproduction of nigraniline and formation of other products. This decomposition occurs still more rapidly in the presence of acids, following a similar course to nigraniline, which, together with *p*-benzoquinone, is first formed. The change is brought about by a few drops of dilute hydrochloric acid, and also more slowly by acetic acid. Reducing agents, if applied at once, convert pernigraniline first into nigraniline, then into emeraldine, and finally into leucoemeraldine. The base is soluble in pyridine, with a purple colour, and apparently undergoes decomposition in this solvent in the same manner as do emeraldine and nigraniline. In concentrated sulphuric acid, it dissolves with a bluish-violet colour. On pouring this solution into water, a green precipitate of emeraldine sulphate is produced.

On account of its instability, pernigraniline cannot be obtained pure in the dry state; an almost complete reversion to nigraniline occurs during drying. An attempt was therefore made to submit it, without drying, to analysis by reduction, employing a paste which contained 8·45 per cent. of dry product. This was prepared as follows. Five grams of the mixture of emeraldine and nigraniline base obtained by the chlorate method were dissolved in 500 c.c. of 80 per cent. acetic acid. To the ice-cold solution was added 5 grams of ammonium persulphate dissolved in a little water, when a violet precipitate at once separated. The whole was then immediately stirred into an excess of dilute ammonia mixed with crushed ice, the temperature being kept as low as possible. After adding a little salt, the precipitate was collected, washed with several litres of water, and brought to a uniform consistency, in which the percentage of water was estimated. The following results were obtained on analysis:

No. of experiment.	Weight of pernigraniline paste (8·45 per cent.) grams.	Vol. of $TiCl_3$ run in (1 litre = 0·0507 gram of hydrogen), c.c.	Vol. of $TiCl_3$ left unoxidised, c.c.	Vol. of $TiCl_3$ oxidised by air, c.c.	Percentage of hydrogen on dry pernigraniline.
1	0·9565	50	34·7	0·28	0·949
2	1·1782	50	31·8	0·25	0·914
3	0·8900	50	36·4	0·29	0·896
4	1·8010	50	24·9	0·20	0·830

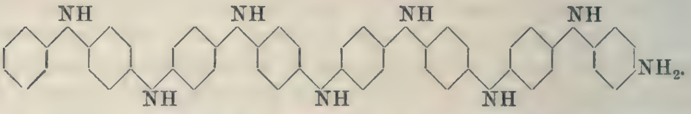
A tetraquinonoid compound of the above constitution would require for reduction to leucoemeraldine 1·11 per cent. of hydrogen. It will therefore be seen that, whilst the first titration gives a value approaching that required by this formula, there is a steady diminution in the consumption of hydrogen in the later analyses. The last titration, which was made after the paste had been kept a day, gives a hydrogen value almost corresponding with that of nigraniline (theory, 0·835 per cent.).

The above formula for pernigraniline is also supported by the figures given on p. 2396 for the consumption of chromic acid required to oxidise emeraldine and nigraniline to pernigraniline chromate. Thus, calculating the whole chromic acid as oxygen, the results are:

	Oxygen consumed, per cent.	$C_{48}H_{34}N_8 + \frac{1}{2}CrO_3$ requires, per cent.
From emeraldine.........	6·13	5·96
,, nigraniline	3·98	3·79

It will be seen that the above formula for pernigraniline is the same as that assigned by Willstätter and Dorogi to the preparations which they call "tetraquinonoid aniline-black." The great instability of pernigraniline is, however, entirely inconsistent with the assumption that these products are identical, since the treatment to which Willstätter and Dorogi's preparations were subjected would have completely decomposed pernigraniline, and even the drying alone, without treatment with acid, would have converted it into nigraniline.

Leucoemeraldine.



This product is readily prepared by reducing either emeraldine or nigraniline with a strong reducing agent. For instance, the mixture of emeraldine and nigraniline bases obtained by the chlorate oxidation was moistened with alcohol in a mortar, and then ground to a paste with a concentrated solution of sodium hyposulphite and a little ammonia. The precipitate was collected, washed, and dried in a vacuum.

A better method consists in moistening the dry base with pure dry ether, and grinding the paste with an equal weight of phenylhydrazine. It is then thrown on a filter, and washed with dry ether until the excess of phenylhydrazine is removed, after which the product is dried quickly on a porous plate.

Leucoemeraldine forms a pale brown, amorphous powder, probably colourless when pure, which does not melt below 350°. It is fairly stable when dry, but when exposed to air in a damp state it becomes blue. It is insoluble in most solvents, but dissolves to a slight extent in pyridine. In 80 per cent. acetic acid or in 60 per cent. formic acid, it is sparingly soluble.

The constitution assigned to leucoemeraldine above is supported by the fact that four atoms of hydrogen are required for its formation from emeraldine, and six atoms for its formation from nigraniline.

Willstätter and Dorogi's Blacks.

In order to ascertain how far the products examined by these authors, and termed "triquinonoid aniline-black" and "tetraquinonoid aniline-black," compare in properties with the foregoing compounds, we have prepared them by following exactly the prescriptions given. The properties of the products we obtained are given in the following table:

Product.	80 per cent. acetic acid.	60 Per cent. formic acid.	Pyridine.
Persulphate Black. (W. & D.)	Considerable portion soluble with bright bluish-green colour.	Partly soluble with bright green colour.	Considerable portion soluble with deep blue colour.
Bichromate Black. (W. & D.)	As above.	As above.	As above.
Chlorate Black : triquinonoid, 6 hours. (W. & D.)	Small part soluble with dull greenish colour.	Nearly insoluble.	Trace only soluble with pale blue colour.
Chlorate Black : triquinonoid, 23 hours. (W. & D.)	Trace soluble with dull greenish colour.	Insoluble.	Very sparingly soluble with pale blue colour.
Chlorate Black : tetraquinonoid, 6 hours. (W. & D.)	Small part soluble with dull greenish colour.	Insoluble.	As above.
Chlorate Black: tetraquinonoid, 22 hours. (W. & D.)	Sparingly soluble with greenish colour.	Very sparingly soluble.	As above.

It will thus be seen that these products differ entirely from the emeraldine, nigraniline, and pernigraniline described above. They appear to be mixtures containing emeraldine, together with further condensation products. Three of them were submitted to successive extractions with cold 80 per cent. acetic acid until nothing further dissolved. The following were the results obtained:

	Persulphate Black (W. & D.), per cent.	Bichromate Black (W. & D.), per cent.	Chlorate Black : triquinonoid (W. & D.), per cent.
Soluble portion	51·5	60·0	80·0
Insoluble portion ...	48·5	40·0	20·0

Oxidation of o-*Toluidine.*

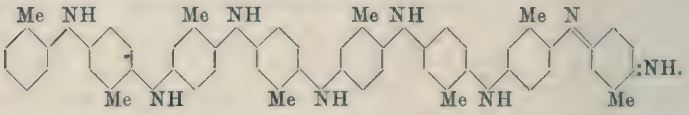
It has long been known to technologists that *o*-toluidine, when oxidised on the fibre, gives rise to a black which is not so brilliant as aniline-black, but which has less tendency to "green." No attempt has apparently been made to prepare this dye or its intermediate compounds in substance.

We have found that under the same conditions as employed for aniline the oxidation proceeds in an analogous manner, giving corresponding products. It appears, however, that the primary oxidation products are rather less stable than in the aniline series, being more prone to undergo polymerisation, and that the higher quinonoid products are less easily formed, and more readily revert to the lower. The best results were obtained by conducting the oxidation without any excess of mineral acid. Thus, 33 grams of *o*-toluidine and 34 grams of hydrochloric acid (33 per cent.) were dissolved in 700 c.c. of water, with the addition of 16·8 grams of sodium chlorate and 2 drops of syrupy vanadium chloride. After being kept for three days at the ordinary temperature, the greenish-blue precipitate was collected, washed with water, basified with ammonia, and then repeatedly extracted with 90 per cent. alcohol in order to remove a soluble by-product (? homologue of Willstätter's blue imide). It was then dried at 30—35°. The product is a violet-blue powder of indigo-like appearance. It is insoluble in most solvents, but dissolves readily in pyridine with a blue colour, and in 80 per cent. acetic acid or 60 per cent. formic acid with a dull yellowish-green colour. It contains 4·6 per cent. of water and 2·0 per cent. of chlorine.

The analysis by reduction was effected in the same manner as employed for emeraldine.

No. of experiment.	Vol. of $TiCl_3$ run in, c.c.	Vol. of $TiCl_3$ unoxidised, c.c.	Vol. of $TiCl_3$ oxidised by air, c.c.	Hydrogen value of 1 litre $TiCl_3$, gram.	Percentage on pure dry substance.
1	50	45·43	0·36	0·0506	0·228
2	50	45·15	0·36	0·0506	0·243
3	50	44·71	0·36	0·0506	0·267
4	50	44·89	0·36	0·0506	0·257
5	50	45·88	0·37	0·0506	0·203
6	50	45·25	0·36	0·0506	0·238
				Mean.........	0·239

A monoquinonoid compound of the constitution:



would require 0·24 per cent. of hydrogen for reduction to the leuco-compound. It therefore appears that the product of the oxidation of *o*-toluidine is the protoemeraldine of this series.

Another preparation in which an excess of acid was used in the oxidation gave as the average consumption of hydrogen for reduction 0·360 per cent. This preparation was therefore apparently a mixture of the tolu-protoemeraldine with tolu-emeraldine.

Attempts to oxidise tolu-protoemeraldine into a higher oxidation stage by means of hydrogen peroxide and ammonia, employing the same conditions as those used for nigraniline, gave a negative result. The product still dissolved in acetic acid with a green colour, and afforded the same reduction figures as before. On the other hand, on addition of chromic acid or persulphate to the acetic acid solution, the colour first becomes blue and then violet, as in the aniline series. It therefore appears that the formation of the tolu-nigraniline does not take place with the same facility as with the lower homologue, a conclusion which is supported by the fact that no tolu-nigraniline was ever produced in our experiments with the chlorate and vanadium oxidation.

Oxidation of Other Amines.

The oxidation of various primary amines was studied under the same conditions as employed in the preparation of emeraldine. *o*-Chloroaniline gave emeraldine-like products; *m*-chloroaniline gave none. *o*-Anisidine underwent oxidation in a different direction, apparently through elimination of the methyl groups. Dimethylaniline remained unattacked.

Conclusions.

1. There are four quinonoid stages derived from the parent compound leucoemeraldine.
2. The minimum molecular weights of these primary oxidation products of aniline are in accordance with an eight-nucleal structure.
3. The conversion of emeraldine into nigraniline consumes one atom of oxygen.
4. The conversion of emeraldine into pernigraniline consumes two atoms of oxygen.
5. The conversion of nigraniline into pernigraniline consumes one atom of oxygen.
6. The reduction of emeraldine to leucoemeraldine consumes four atoms of hydrogen.
7. The reduction of nigraniline to leucoemeraldine consumes six atoms of hydrogen.
8. The reduction of pernigraniline to leucoemeraldine consumes eight atoms of hydrogen.
9. The reduction of tolu-protoemeraldine consumes two atoms of hydrogen.
10. None of these products are properly entitled to be considered as aniline-black, but are intermediate products in the formation of the latter.

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CCXLIV.—*Chloroamine Reactions. Methylene-chloroamine.**

By Charles Frederick Cross, Edward John Bevan, and William Bacon.

Chloroamine, NH_2Cl, although not yet isolated, has been closely characterised by its reactions in solution. Raschig (*Ber.*, 1907, **40**, 4586) has verified the above formula by the synthesis of hydrazine according to the equation:

$$NH_2Cl + NH_3 = H_2N{\cdot}NH_2,HCl.$$

In oxidising actions, the chloroamine chlorine reacts as the chlorine of hypochlorites, thus:

$$NH_2Cl + 2HI = NH_4Cl + I_2,$$

from which, and in view of its formation by interaction of hypochlorites and ammonium salts, it might be formulated as NH_4OCl.

From a general view of its oxidising reactions, however, these are found in many and typical cases to be sharply differentiated from those of the hypochlorites, and hence its formation from hypochlorites is rather represented by the equation:

$$NH_3 + M{\cdot}OCl = NH_2Cl + M{\cdot}OH.$$

It may be inferred from Raschig's investigations that such reactions would be a general characteristic of amino-compounds, and we have studied certain of these in relation to their conversion into chloroamines.

As a result, we have been able to characterise the compounds obtained from proteins by the action of chlorine as chloroamines (Cross, Bevan, and Briggs, *J. Soc. Chem. Ind.*, 1908, **27**, 260).

Such compounds have been known since 1840 (Mulder, *Berzelius' Jahresber*, **19**, 734), and their formation has been made the basis of quantitative analytical methods (Rideal and Stewart, *Analyst*, 1897, **22**, 228), depending on the separation of these derivatives, which are insoluble in water, followed by nitrogen estimations in the precipitated compounds. These methods we find are much simplified by estimations of chloroamine chlorine according to the well-known chlorimetric methods.

We have described such methods in detail as applicable to the estimation of gelatin, and we have also applied similar reactions to the elucidation of industrial processes which are attended by the formation of chloroamines, notably the bleaching of flax textiles (*loc. cit.*).

In the case of gelatin it is noteworthy that the chloroamine derivative is of constant composition, the chloroamine chlorine ($=Cl_2$) representing 18·3 per cent. of original gelatin, and after dehydration is stable in the air.

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* This name is retained pending the final settlement of the constitution of the compound, in order to indicate its relation to chloroamine.

Methylenechloroamine.

The typical reactions of chloroamine, especially with aromatic amines and phenols, have further been elucidated by Raschig (*Chem. Zeit.*, 1907, **31**, 126; *Zeitsch. angew. Chem.*, 1907, **20**, 2065).

In extending these investigations, we have observed a reaction of special interest which we will briefly describe, as it involves a new chloroamine, readily obtainable in crystalline form.

Formaldehyde and chloroamine in aqueous solution react according to the equation:

$$CH_2O + H_2NCl = CH_2\colon NCl + H_2O,$$

the resulting methylenechloroamine separates in well-formed crystals, and on recrystallisation from chloroform, in which it is easily soluble, it is obtained in needles of 10 to 15 mm. in length. To prepare this compound, approximately semi-normal solutions of hypochlorites ($Cl = 1·8$ grams per 100 c.c.) are treated with ammonium chloride, and formaldehyde solution added in the cold. The proportions are taken somewhat in excess of the calculated. On keeping at, or under, 15°, the solution becomes milky, and the compound then crystallises. It is obtained as a mass of brilliant, felted needles. The yields under these conditions are 30 to 40 per cent. of the calculated.

For analysis, the substance is dissolved in chloroform, the solution being left for some hours in contact with calcium chloride, and poured off through a dry filter, when, after some time, the substance crystallises out.

Many preparations have been analysed, and the numbers are in close accordance with the formula CH_2NCl.

The following results are typical:

Total chlorine, by digestion with sodium sulphite and precipitation as silver chloride:

0·1255 gave 0·2815 AgCl.

"*Active chlorine*," by digestion with potassium iodide solution and titration of the liberated iodine:

0·3124 liberated $I = 99·8$ c.c. *N*/10-thiosulphate.

Nitrogen, by digestion with ferrous sulphate, in presence of sulphurous acid, and distillation from alkalis; the nitrogen being obtained as ammonia:

0·1135 gave $NH_3 = 18·2$ c.c. *N*/10-HCl.

Found, Total $Cl = 55·4$; "Active" $Cl = 56·7 \times 2$; $N = 22·4$.

CH_2NCl requires Total $Cl = 55·9$; "Active" $Cl = 55·9 \times 2$; $N = 22·05$ per cent.

Molecular-weight determinations even by cryoscopic methods present difficulties, due to the instability and reactivity of the compound, but the following numbers calculated from the depression of the freezing point of benzene were obtained:

Found, M.W. = 133·0, 132·7, 131·7.

$2CH_2NCl$ requires M.W. = 127.

Our incidental observations indicate a change of solubility in benzene from 2·7 to 1·5 per 100 c.c. at 5°, and polymerisation probably has to be taken into account. This point will be resolved by further investigation.

Methylenechloroamine is soluble in 20 to 30 parts of ether at the ordinary temperature, and similarly in benzene, as indicated above; it is only sparingly soluble in paraffinoid hydrocarbons.

It decomposes spontaneously in ordinary air, and when heated at 50—60° it decomposes explosively, leaving a residue of ammonium chloride.

As shown by the analytical results, it may be quantitatively hydrolysed and reduced, ammonia and formaldehyde being regenerated, and by certain decompositions it yields hydrocyanic acid as a main product

The investigation is being continued.

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CCXLV.—*Narcissine: an Alkaloid from the Bulb of the Common Daffodil (Narcissus pseudonarcissus).*

By Arthur James Ewins.

In 1878 a paper was published by Ringer and Morshead (*J. Physiol.* **1**, 437), entitled "On the physiological action of narcissia, an alkaloid obtained from the bulb of the common daffodil (*Narcissus pseudonarcissus*)." This work contained a detailed account of experiments carried out on men and frogs with an alkaloid or with extracts containing the alkaloid, which had been obtained by Gerrard from the bulb of the common daffodil. From experiments carried out with extracts obtained from bulbs in the resting stage and from bulbs of the flowering plants, the authors concluded that the action of the alkaloid present in the extracts from the resting bulbs was similar to that of pilocarpine, whereas that present in the extracts from the bulbs of the flowering plants closely resembled atropine in action. The alkaloid obtained by Gerrard from both extracts nevertheless appeared to be the same in general chemical properties.

In view of these statements and of the fact that no reference to "narcissia" or to any alkaloid obtained from the bulbs of the daffodil can be found in chemical literature, it appeared to be of interest to obtain the alkaloid in a pure state, in order that a more detailed investigation of its chemical and physiological properties might be made, more especially as the alkaloids which have been obtained from monocotyledons are comparatively few in number.

The bulbs of a cultivated variety of the daffodil (*Narcissus princeps*), being more readily obtainable than the variety mentioned above, were first employed in the investigation. From these bulbs, however, the extracts obtained from the resting or flowering bulbs gave only traces of alkaloidal reactions, and the isolation of the alkaloid was obviously hopeless. With the bulbs of the wild daffodil (*Narcissus pseudonarcissus*), much more satisfactory results were obtained. From these a crystalline alkaloid was readily obtained. From the resting bulbs a yield of approximately 0·2 per cent. of the dried material, and from the flowering bulbs only about 0·1 per cent., was obtained. The alkaloid, which, in accordance with modern usage, it is suggested be called "narcissine," rather than "narcissia," was the same in both cases.

Narcissine has been found by analyses and molecular-weight determination to possess the formula $C_{16}H_{17}O_4N$. The alkaloid is characterised by very great stability, and on that account and owing to the small amount of material available (about 3 grams only), no light has been thrown on its probable constitution. The nitrogen present is tertiary, since nitrous acid is without action on the alkaloid, and treatment with methyl iodide produced an amorphous product which was probably the methiodide of the base, but which could not be crystallised for analysis. The action of hydriodic acid (Zeisel) showed the absence of methoxy-groups, but on very strongly heating, a very small amount of methyl iodide was evolved, and the residue on suitable treatment yielded a solution which gave a violet coloration with ferric chloride, the phenolic substance being extracted from its acid solution by ether. The amount of substance so obtained was, however, extremely small, and further attempts to hydrolyse by means of acids yielded no crystalline product.

Fusion with potassium hydroxide yielded no better results. At temperatures up to 220° the alkaloid was only very slowly attacked, traces of alkaline vapour being evolved. Heating with the naked flame for one and a-quarter hours was required in order to decompose completely about 0·7 gram of the alkaloid. The reaction product dissolved in water gave on addition of ferric chloride a violet coloration, quickly passing to a dirty brown, with separation of a brown, flocculent precipitate. This polyphenolic substance, again, could be extracted by ether from its acid solution, but on evaporating off the solvent only a very small quantity of a brown, amorphous product was obtained, and all attempts to obtain a crystalline product were fruitless.

On account of the relatively large number of oxygen atoms present in the molecule, it was thought possible that a carboxyl group might be present, but attempted esterification showed the absence of such grouping. For this reason and from the absence of methoxy-groups as shown by the Zeisel reaction, the formation of a polyphenolic derivative such as has been described is very possibly due to the presence in the molecule of a methylenedioxy-grouping and a phenolic bridge oxygen. The stability of the alkaloid would seem to support such a view, although there is, of course, no direct evidence of such structure.

Experiments with regard to the physiological action of the alkaloid were carried out in these laboratories by Dr. P. P. Laidlaw, to whom I am indebted for the following account of its action. As tested on frogs and cats, the alkaloid showed no action in any way similar to that of pilocarpine or of atropine. 0·125 Gram, given by mouth to a cat, caused nausea, vomiting, salivation, and purgation. The salivation was not, however, similar to that produced by pilocarpine, since it could not be produced on the anæsthetised animal.

EXPERIMENTAL.

Preparation of the Alkaloid.

Two thousand five hundred bulbs of the common daffodil (*Narcissus pseudonarcissus*), weighing approximately 4 kilos., were dried at a temperature of about 40°. The weight of the dried product was 1400 grams. The substance was finely ground and extracted for about six hours with hot alcohol (97 per cent.), and the alcoholic extract evaporated to about 200 c.c. To the dark syrupy, acid liquid was added an equal volume of water, and a very dark resinous precipitate which formed was collected. This precipitate was re-suspended in a little very dilute acid, and again collected after thoroughly shaking. The filtrate and washings were combined, and the acid liquid extracted twice with about one-third of its volume of ether. The aqueous solution was then rendered alkaline by addition of sodium carbonate, when, after some time, a precipitate formed, which consisted mainly of bunched prisms. The crystals were collected, and after recrystallisation from 90 per cent. alcohol were obtained as colourless, short, stout prisms, melting at 266—267° (bath at 250° at commencement of heating). The substance was dried first in air, then in a vacuum over sulphuric acid, and finally at 110°, no alteration in weight taking place under these varying conditions:

0·1448 gave 0·3552 CO_2 and 0·0754 H_2O. C = 66·9; H = 5·8.
0·1283 „ 0·3159 CO_2 „ 0·0684 H_2O. C = 67·1; H = 5·9.
0·1051 „ 5·0 c.c. N_2 (moist) at 13·5° and 732 mm. N = 5·4.
$C_{16}H_{17}O_4N$ requires C = 66·9; H = 5·9; N = 5·0 per cent.

A determination of the molecular weight was made by Barger's microscopic method (Trans., 1904, **86**, 286) in glacial acetic acid. 0·060 Gram, in 1·197 grams of solvent, was intermediate between 0·19 mol. and 0·20 mol., whence M.W. = 257. $C_{16}H_{17}O_4N$ requires M.W. = 287.

Properties of Narcissine.—The alkaloid, as before stated, is obtained by recrystallisation from alcohol in colourless prisms, which melt at 266—267° with some decomposition and formation of a red liquid. The crystals are insoluble in water or dilute sodium hydroxide, but readily soluble in dilute acid. The acid solution gives all the usual alkaloidal reactions, for example, with Meyer's reagent, with a solution of iodine in potassium iodide, and with phosphotungstic acid. The crystalline product is only very sparingly soluble in methyl alcohol, ethyl alcohol, ethyl acetate, or acetone, moderately so in pyridine, nitrobenzene, or glacial acetic acid, and insoluble in ether or chloroform. A determination of its solubility in absolute ethyl alcohol showed that one part by weight of the alkaloid was soluble in 284 parts of boiling alcohol and in 340 parts of alcohol at 15°.

The alkaloid is lævorotatory. 0·166 Gram, made up to 100 c.c. with absolute alcohol, gave, in a 2·2-dcm. tube at 10°, α_D −0·35°, whence $[\alpha]_D^{10}$ −95·8°.

The alkaloid dissolves in concentrated sulphuric acid, producing a deep red solution, which slowly becomes reddish-brown on keeping.

Narcissine Hydrochloride, $C_{16}H_{17}O_4N,HCl$.—0·3 Gram of crude narcissine was dissolved in dilute hydrochloric acid, and the solution evaporated to dryness over potassium hydroxide in a desiccator. The resulting crystalline product was dissolved in hot 90 per cent. alcohol, and after treatment with a little blood-charcoal, the solution, on cooling, deposited the hydrochloride in long, thin prisms, melting at 198—199°. Yield, 0·27 gram:

0·2737 gave 0·1176 AgCl. Cl = 10·6.
$C_{16}H_{17}O_4N,HCl$ requires Cl = 10·9 per cent.

THE WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES,
HERNE HILL, S.E.

CCXLVI.—*The Action of Halogens on Mercuricamphor Compounds.*

By JAMES ERNEST MARSH.

THE work described in this paper is a continuation of that published by Mr. Struthers and the author on the mercury derivatives of camphor (Trans., 1909, **95**, 1777).

In the former paper it was shown that di-iodocamphor was obtained by the action of iodine on one of the mercury derivatives. It is now found that the same di-iodocamphor is formed from the three mercury compounds, namely, those which have the formulæ: $C_{10}H_{14}OHg_2I_2$, $(C_{10}H_{14}O)_3Hg_4I_2$, and $(C_{10}H_{14}O)_4Hg_5I_2$. The method of preparation is the same in each case The mercury compound is treated with an aqueous solution of iodine and potassium iodide, enough iodine being taken to combine with the mercury and the camphor residue, and enough potassium iodide to hold the mercuric iodide in solution. The product of the reaction is extracted with chloroform, and the chloroform solution washed with sodium hydroxide, dried, and rapidly evaporated. The di-iodocamphor is then left in the crystalline form, and, after washing with light petroleum, is practically pure. A small amount of camphorquinone, which is formed, is removed by the petroleum. If the operation is carried out carefully, the yield is nearly quantitative, but if the substance is left too long in the chloroform solution the amount obtained is less satisfactory, as it decomposes in solution. Even when the substance is partly decomposed by being overheated or left too long in solution, a good product can still be obtained by boiling with sodium hydroxide solution, and washing the residue with petroleum. Di-iodocamphor, when in solution, rapidly decomposes with separation of iodine. In order to recrystallise it, the best solvent was found to be aqueous pyridine. It is very soluble in pure pyridine, and, on adding a little water, crystals at once separate. The crystals should be spread out in a thin layer to dry, as they rapidly decompose if heaped up in masses while still wet with the solvent. The compound decomposes a little above its melting point, 108°, with evolution of iodine. It is stable in presence of alkalis, and may be kept under a solution of sodium hydroxide. It may be boiled with aqueous sodium hydroxide without decomposition, and it is not appreciably volatile in steam.

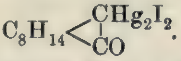
Action of Oxygen on Di-iodocamphor. Camphorquinone.

Although in the crystalline form, di-iodocamphor is stable when exposed to air, when dissolved in chloroform it decomposes with separation of iodine. One atom of oxygen takes the place of the two atoms of iodine, and camphorquinone is formed, along with a small quantity of camphoric anhydride.

To obtain camphorquinone in this way, air dried by sulphuric acid is bubbled through a solution of di-iodocamphor in chloroform. Iodine at once begins to separate, as is shown by the change in the colour of the solution. Fresh chloroform is added, when necessary, to make good the loss by evaporation. When the action is finished, the product is mixed with a solution of sodium hydroxide and distilled in a current of steam. The alkali serves not only to combine with the free iodine, but also to convert the camphoric anhydride into sodium camphorate; otherwise the anhydride distils over in the steam, and renders the quinone impure. The quinone appears in the distillate as yellow crystals, and also colours the water yellow. It is extracted with ether or, better, with chloroform. The ethereal extract gave, on evaporation, crystals melting at 196—197°, which, after recrystallisation from alcohol, melted at 198—199°. (Found, $C=71{\cdot}7$; $H=8{\cdot}4$. Calc., $C=72{\cdot}3$; $H=8{\cdot}4$ per cent.)

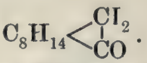
The yield of camphorquinone by this method is more than 90 per cent. of that required by theory. This method should serve for the production of camphorquinone in any quantity from camphor, since the yield of the mercury compound from camphor and that of di-iodocamphor from the mercury compound are both nearly quantitative. Further, all the mercury and iodine employed in the reactions can be recovered in the form of mercuric iodide, and used again for the preparation of the camphor-mercury compound.

Camphorquinone is readily oxidised to camphoric acid by warming with a solution of sodium peroxide; the crystals dissolve, and the yellow colour of the solution disappears; on acidifying, camphoric acid, melting at 186°, separates. It is converted by the action of acetyl chloride into camphoric anhydride, melting at 220°. This conversion of di-iodocamphor into camphorquinone and camphoric acid shows that the iodine has replaced the hydrogen in the CH_2 group, which is adjacent to the CO group. It also shows further that, in the mercury derivatives, the Hg'' and $(HgI)'$ groups are similarly situated in the $\alpha\alpha'$-position. This was anticipated by Mr. Struthers and myself from the circumstance that the only ketones which we found to give mercury derivatives were those having hydrogen in the α-position. The structural relationship of the mercury and iodine derivatives to camphorquinone is shown by the formulæ:



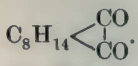
$$C_8H_{14}<\begin{matrix}CHg_2I_2\\ |\\ CO\end{matrix}.$$

Dimercuricamphor di-iodide.



$$C_8H_{14}<\begin{matrix}CI_2\\ |\\ CO\end{matrix}.$$

Di-iodocamphor.



$$C_8H_{14}<\begin{matrix}CO\\ |\\ CO\end{matrix}.$$

Camphorquinone.

Action of Bromine on the Mercuricamphor Compounds.

$\alpha\alpha'$-Dibromocamphor.

The action of bromine on the mercuricamphor compounds is not so simple as is the action of iodine. In the main, the reaction proceeds with the production of $\alpha\alpha'$-dibromocamphor, melting at 61°. The action is, however, complicated by liberation of iodine and its action, also by the oxidising action of the bromine, and further by the action of the hydrogen bromide produced in the oxidation.

To prepare $\alpha\alpha'$-dibromocamphor, the mercury compound $(C_{10}H_{14}O)_4Hg_5I_2$ is preferably employed, since it contains less iodine than the other mercuricamphor compounds.

The mercuricamphor compound is mixed with half its weight of powdered mercuric oxide, and this mixture is added gradually to a solution in water of the requisite amounts of bromine and potassium bromide, so that the whole of the mercuric bromide formed is dissolved in the water. The mixture is stirred all the time with a turbine, and it becomes warm as the reaction proceeds. When cold, the mixture is extracted with chloroform. The chloroform solution is washed with sodium hydroxide and water, dried, and evaporated. The crude dibromocamphor left on evaporation is purified by solution in light petroleum. The petroleum solution is filtered, if necessary, from a small quantity of a crystalline substance, which is referred to later. On evaporation of the petroleum, the residue is distilled under diminished pressure. $\alpha\alpha'$-Dibromocamphor distils at about 175°/20 mm., and solidifies in the receiver. After recrystallisation from alcohol, it melted at 61°. (Found, $Br = 51{\cdot}5$. Calc., $Br = 51{\cdot}6$ per cent.)

Mr. T. V. Barker examined the crystals with the goniometer, and found the measurements to be identical with those given by Zepharowich for $\alpha\alpha'$-dibromocamphor.

By its production in this way, the dibromocamphor is brought into relationship with di-iodocamphor, camphorquinone, and camphoric acid; hence its constitution as an $\alpha\alpha'$-compound is confirmed.

The same dibromocamphor is produced by the action of bromine in chloroform instead of aqueous solution. It is also obtained from the mercury compound $C_{10}H_{14}OHg_2I_2$, and by the action of bromine on di-iodocamphor in chloroform solution. It may be presumed to be also obtainable, like di-iodocamphor, from the intermediate mercury compound $(C_{10}H_{14}O)_3Hg_4I_2$.

The use of mercuric oxide in the preparation of dibromocamphor needs some explanation. It was found to prevent the formation of by-products. It probably acts by combining with any hydrogen bromide which may be formed, and thus preventing the decomposition of the mercuricamphor compound into camphor and mercuric bromide.

The crystalline compound insoluble in petroleum is obtained when mercuric oxide is not employed in the reaction; and at the same time some α-monobromocamphor is formed. The former substance crystallised well from alcohol, and melted at 159°. Numerous analyses were made of this substance, prepared under varying conditions. The analyses do not indicate the presence of a single substance, but of a mixture intermediate between the compounds $C_{10}H_{14}O_2Br_2$ and $C_{10}H_{14}O_2I_2$, with no simple relation between the bromine and the iodine atoms. When bromine acts on di-iodocamphor, a similar substance is formed with relatively more iodine and less bromine in its composition, and of a higher melting point, namely, 172°. A product of a similar nature is obtained with chlorine taking the place of bromine, when a chloroform solution of di-iodocamphor is acted on by chlorine.

When the mercuricamphor compound is treated with iodine bromide, IBr, or by iodine chloride, ICl, the principal product in each case is di-iodocamphor.

I wish to thank my assistant, Mr. F. Hall, for his excellent help in this investigation.

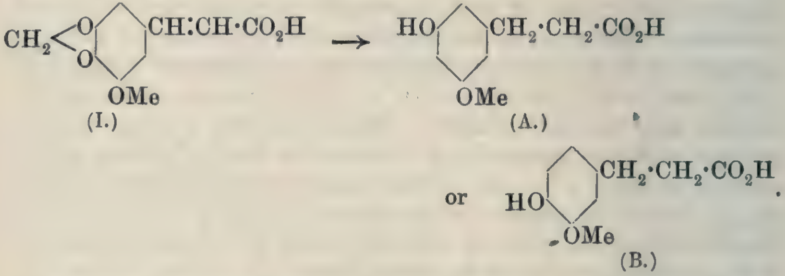
University Laboratory,
Oxford.

CCXLVII.—*Action of Sodium Amalgam on Methylene Ethers.*

By Arthur Henry Salway.

In the course of the author's previous investigations, which led to the synthesis of cotarnine (Trans., 1909, **95**, 1204; this vol., 1208), the reduction of 3-methoxy-4:5-methylenedioxycinnamic acid (I) was described. In this reaction it was observed that the normal reduction product, namely, β-3-methoxy-4:5-methylenedioxyphenylpropionic acid (II), was invariably accompanied by a considerable proportion of a by-product. This substance, of which no account was given in the previous communications, has now been isolated in sufficient quantity to render its complete examination possible.

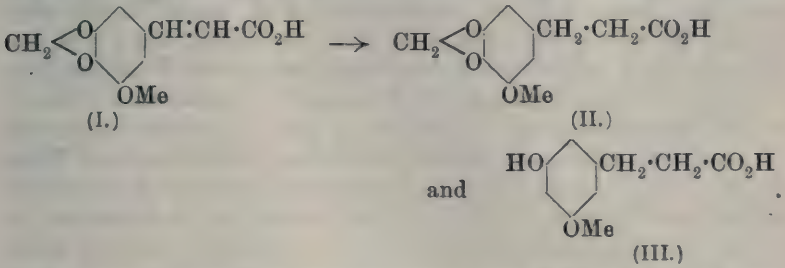
The purified compound was found to possess the properties of a phenol and of a carboxylic acid, and gave analyses corresponding with the empirical formula $C_{10}H_{12}O_4$. It is evident that the production of such a compound from 3-methoxy-4 : 5-methylenedioxycinnamic acid (I) can only be explained by the simultaneous reduction of the aliphatic side-chain and the substitution of a hydroxyl group for the methylenedioxy-complex. The constitution of the resulting compound would therefore appear to be represented by one of the two formulæ A and B:



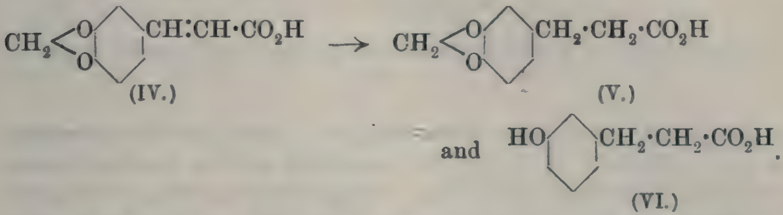
(I.) (A.) (B.)

In order to decide between these formulæ, the substance was converted by means of methyl sulphate into a dimethoxyphenylpropionic acid, which melted at 61—62°. The dimethoxy-acid corresponding with B, namely, β-3 : 4-dimethoxyphenylpropionic acid, melts, according to Tiemann and Nagai (*Ber.*, 1878, **11**, 653), at 97°, whilst the 3 : 5-dimethoxy-acid corresponding with A does not appear to have been hitherto described. Formula B is thus shown to be inadmissible, and consequently A most probably represents the constitution of the substance under examination. Positive evidence in support of this conclusion was obtained by converting the dimethoxypropionic acid into the corresponding dimethoxybenzoic acid by oxidation with alkaline permanganate solution. The product of oxidation melted at 180—181°, and was found to be identical with 3 : 5-dimethoxybenzoic acid. It is thus shown that in the reduction of 3-methoxy-4 : 5-methylenedioxycinnamic acid (I), the normal reaction is accompanied by a secondary change involving the disruption of the methylenedioxy-complex and the formation of β-5-hydroxy-3-methoxyphenylpropionic acid (III), according to the scheme on p. 2415.

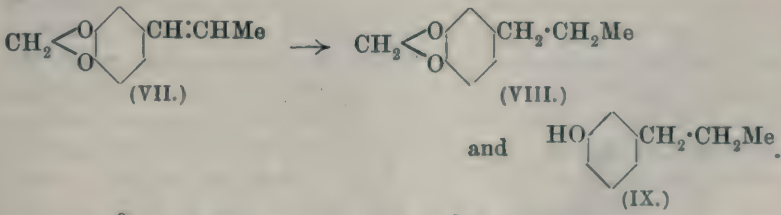
It was next deemed of interest to ascertain whether other methylene ethers are capable of undergoing a similar change, and accordingly piperonylacrylic acid (IV) was subjected to the action of sodium amalgam. In this case, also, it was found that reduction takes place with partial conversion of the methylenedioxy-complex into a hydroxyl group, the products of the reaction being a mixture

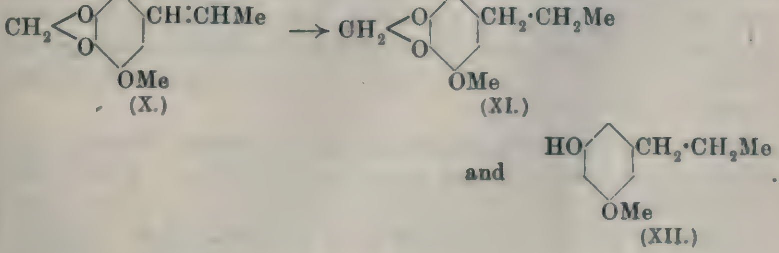

(I.) (II.) and (III.)

of β-3 : 4-methylenedioxyphenylpropionic acid (V) and β-3-hydroxyphenylpropionic acid (VI):


(IV.) (V.) and (VI.)

A similar reaction has been observed by Ciamician and Silber (*Ber.*, 1890, **23**, 1162), who have shown that *iso*safrole (VII), when reduced by sodium and alcohol, is converted into a mixture of 3 : 4-methylenedioxypropylbenzene (VIII) and *m*-propylphenol (IX), whilst Thoms (*Ber.*, 1903, **36**, 3449) records the fact that *iso*myristicin (X), under similar conditions, yields both 5-methoxy-3 : 4-methylenedioxypropylbenzene (XI) and 5-methoxy-3-propylphenol (XII):


(VII.) (VIII.) and (IX.)


(X.) (XI.) and (XII.)

It is worthy of note that in each of the above examples of the displacement of a methylenedioxy-complex by a hydroxyl group, the latter appears in the meta-position with regard to the side-chain. Moreover, the position of the unsaturated linking in the side-chain is of importance in determining the course of the reaction, since only those compounds which contain the unsaturated linking in the $\alpha\beta$-position with regard to the benzene nucleus appear to be capable of undergoing the above-described transformation. Thus, for example, the methylenedioxy-group of *iso*myristicin (X) is readily decomposed by means of sodium and alcohol, whilst myristicin, in which the unsaturated linking is in the $\beta\gamma$-position, does not suffer this change.

EXPERIMENTAL.

Reduction of 3-Methoxy-4 : 5-methylenedioxycinnamic Acid (I, p. 2415).

A solution of one part of 3-methoxy-4 : 5-methylenedioxycinnamic acid in 20 parts of 1 per cent. aqueous sodium hydroxide was reduced by the gradual addition, with constant stirring, of 16 parts of sodium amalgam (4 per cent.). After the amalgam had been completely decomposed, the mixture was acidified, the precipitated oil extracted with ether, and the ethereal solution washed, dried, and the solvent removed. In this manner the product of reduction was obtained as a light brown oil, which gradually became crystalline. A preliminary examination of the product indicated the presence of a considerable proportion of a phenolic carboxylic acid in addition to the normal reduction product, β-3-methoxy-4 : 5-methylenedioxyphenylpropionic acid. In order to effect a separation of these compounds, the mixture was dissolved in alcohol and esterified by means of dry hydrogen chloride, after which the excess of alcohol was removed and the esters extracted with ether. The ethereal solution was first washed with aqueous sodium carbonate to remove any unesterified acid, and then shaken with dilute sodium hydroxide. The sodium hydroxide extract, which contained the phenolic ester, was warmed for a short time to complete the hydrolysis of the latter, then acidified and extracted with ether. This ethereal extract yielded a colourless solid, which was recrystallised from hot water, when it separated in flat, hexagonal plates, melting at 127°:

0·1103 gave 0·2482 CO_2 and 0·0635 H_2O. C = 61·4; H = 6·4.

0·2800 required for neutralisation 14·35 c.c. $N/10$-KOH. M.W. = 195.

$C_{10}H_{12}O_4$ requires C = 61·2; H = 6·1 per cent. M.W. = 196.

As already explained in the introduction, this substance was found to be β-5-hydroxy-3-methoxyphenylpropionic acid.

β-5-*Hydroxy*-3-*methoxyphenylpropionic acid* (III, p. 2415) is readily soluble in ether, alcohol, or hot water, and crystallises from the latter in colourless, hexagonal plates, which gradually become pink on exposure to air. It is insoluble in benzene or light petroleum. Its *amide*, $MeO\cdot C_6H_3(OH)\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2$, crystallises from water in prismatic needles, melting at 126°.

In order to prepare the methyl derivative of the above compound, 10 grams of the phenolic acid were dissolved in methyl alcohol and 5 c.c. of methyl sulphate, and 10 c.c. of a 50 per cent. solution of potassium hydroxide added. After the vigorous reaction had subsided, the same quantities of methyl sulphate and alkali were again added, and the mixture heated for a short time on the water-bath. The alkaline liquid was then acidified and extracted with ether, when the ethereal extract yielded an oil which gradually solidified. This product was purified by crystallisation from a mixture of benzene and light petroleum, from which it separated in clusters of colourless, silky needles, melting at 61—62°:

0·1076 gave 0·2490 CO_2 and 0·0649 H_2O. C = 63·1; H = 6·7.

0·4465 required for neutralisation 21·25 c.c. $N/10$-NaOH. M.W. = 210.

$C_{11}H_{14}O_4$ requires C = 62·9; H = 6·7 per cent. M.W. = 210.

β-3:5-*Dimethoxyphenylpropionic acid*,

$$C_6H_3(MeO)_2\cdot CH_2\cdot CH_2\cdot CO_2H,$$

is readily soluble in the usual organic solvents, excepting light petroleum. It yields an *amide*, which crystallises from a mixture of benzene and petroleum in colourless needles, melting at 80—81°. The position of the methoxy-groups in the above compound was ascertained by oxidising a quantity of the substance with a hot alkaline solution of potassium permanganate. At the end of the oxidation, the liquid was cooled, an excess of sulphur dioxide added, and the precipitated oxidation product collected. It was recrystallised from hot water, when it separated in thin needles, melting at 180—181°. (0·2045 required for neutralisation 11·25 c.c. $N/10$-NaOH. M.W. = 182. Calc., M.W. = 182.)

This substance possessed all the properties of 3:5-dimethoxybenzoic acid (Bülow and Riess, *Ber.*, 1902, **35**, 3901), and was evidently identical with that compound.

Reduction of Piperonylacrylic Acid.

The reduction of piperonylacrylic acid by means of sodium amalgam was first described by Lorenz (*Ber.*, 1880, **13**, 758), who isolated piperonylpropionic acid from the product of the reaction, but did not record the formation of a phenolic compound. In view, however, of the results obtained in the above reduction of 3-methoxy-4 : 5-methylenedioxycinnamic acid, it seemed probable that some β-5-hydroxyphenylpropionic acid would be formed in the reduction of piperonylacrylic acid. In order to ascertain if this were the case, 20 grams of piperonylacrylic acid were reduced with sodium amalgam in the manner described in connexion with the reduction of 3-methoxy-4 : 5-methylenedioxycinnamic acid. The product was then esterified, and, by means of dilute sodium hydroxide, separated into a non-phenolic and a phenolic ester. The former amounted to 18 to 19 grams, and yielded on hydrolysis piperonylpropionic acid, melting at 85°, whilst the latter, when hydrolysed, yielded a brown oil (2 grams), which gradually solidified on agitation with benzene. This substance was purified by recrystallisation from a mixture of ether and benzene, and was thus obtained in colourless needles, melting at 110°. (0·1922 required 11·8 c.c. N/10-NaOH for neutralisation. M.W. = 163. Calc., M.W. = 166.)

This compound possessed all the properties of 3-hydroxyphenylpropionic acid, and was evidently identical with it (Braunstein, *Ber.*, 1882, **15**, 2050).

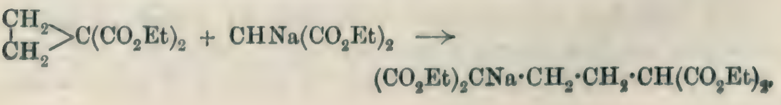
The action of sodium amalgam on piperonylacrylic acid is therefore analogous to that which takes place when 3-methoxy-4 : 5-methylenedioxycinnamic acid is reduced. The yield of phenolic acid in the latter case is, however, much greater than in the former.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

CCXLVIII.—*An Instance Illustrating the Stability of the Four-Carbon Ring.*

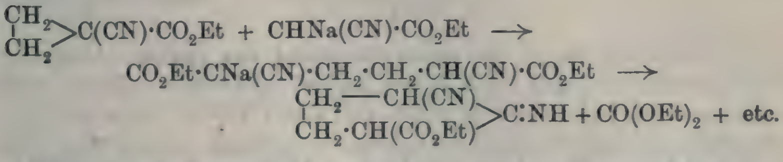
By ARTHUR FRED CAMPBELL and JOCELYN FIELD THORPE.

It has been shown by Bone and Perkin (Trans., 1895, **67**, 108) that when a derivative of *cyclo*propane which has two carbethoxy-groups attached to the same carbon atom is treated with the sodium compound of ethyl malonate, condensation ensues, with the formation of an open-chain ethyl ester in the following way:



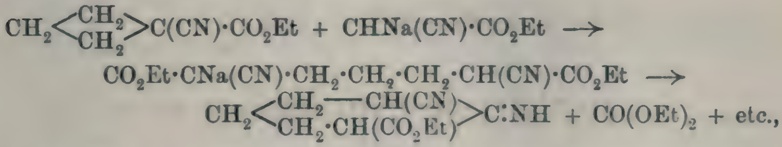
$$\left.\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\right>C(CO_2Et)_2 + CHNa(CO_2Et)_2 \longrightarrow (CO_2Et)_2CNa\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2.$$

This reaction has been made use of by us for the preparation of certain open-chain nitriles (Trans., 1909, **95**, 697; this vol., 1002), which we found possessed the property of readily passing into imino-derivatives of *cyclo*pentane when treated with sodium ethoxide, thus:



$$\left.\begin{matrix}\mathrm{CH_2}\\ |\\ \mathrm{CH_2}\end{matrix}\right>\mathrm{C(CN){\cdot}CO_2Et + CHNa(CN){\cdot}CO_2Et} \longrightarrow$$
$$\mathrm{CO_2Et{\cdot}CNa(CN){\cdot}CH_2{\cdot}CH_2{\cdot}CH(CN){\cdot}CO_2Et} \longrightarrow$$
$$\left.\begin{matrix}\mathrm{CH_2}\text{—}\mathrm{CH(CN)}\\ |\qquad\qquad\\ \mathrm{CH_2{\cdot}CH(CO_2Et)}\end{matrix}\right>\mathrm{C{:}NH + CO(OEt)_2} + \text{etc.}$$

Wishing to prepare the open-chain compound containing one more methylene group, in order to study the conditions under which it passed into a derivative of *cyclo*hexane, we decided to apply the above reaction to ethyl 1-cyano*cyclo*butane-1-carboxylate, in the hope that the following reaction would ensue:



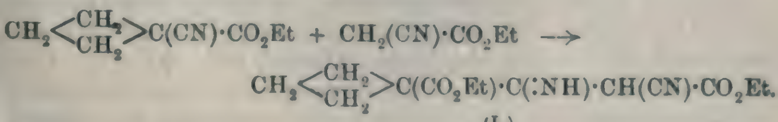
$$\mathrm{CH_2}\left<\begin{matrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{matrix}\right>\mathrm{C(CN){\cdot}CO_2Et + CHNa(CN){\cdot}CO_2Et} \longrightarrow$$
$$\mathrm{CO_2Et{\cdot}CNa(CN){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CN){\cdot}CO_2Et} \longrightarrow$$
$$\mathrm{CH_2}\left<\begin{matrix}\mathrm{CH_2}\text{—}\mathrm{CH(CN)}\\ \mathrm{CH_2{\cdot}CH(CO_2Et)}\end{matrix}\right>\mathrm{C{:}NH + CO(OEt)_2} + \text{etc.,}$$

and that in this way an imino-derivative of *cyclo*hexane would be formed. We found that this condensation yielded considerable quantities of a crystalline substance melting at 111°, which possessed the molecular formula $C_{13}H_{18}O_4N_2$, that is to say, it seemed to be the normal open-chain compound of the formula:

$$\mathrm{CO_2Et{\cdot}CH(CN){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CN){\cdot}CO_2Et.}$$

All attempts, however, to induce it to react with sodium ethoxide proved unavailing, and we consequently decided that the imino-derivatives of the six-membered ring could not be produced in the same manner as those of *cyclo*pentane.

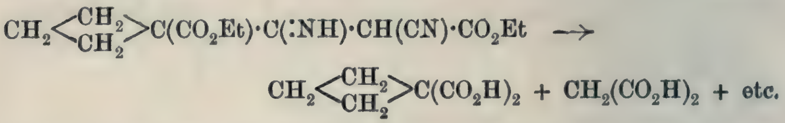
Before recording this fact, we subjected the open-chain compound to complete hydrolysis in order to prove its constitution by the formation of pimelic acid, when it was found that instead of this acid the product consisted of *cyclo*butane-1 : 1-dicarboxylic acid and malonic acid. Subsequent experiments showed conclusively that the condensation product of the formula $C_{13}H_{18}O_4N_2$ was *ethyl β-imino-α-cyano-1-carbethoxy-β-*cyclo*butyl-1-propionate* (I), and that it had been formed in the following manner:



$$\mathrm{CH_2}\left<\begin{matrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{matrix}\right>\mathrm{C(CN){\cdot}CO_2Et + CH_2(CN){\cdot}CO_2Et} \longrightarrow$$
$$\mathrm{CH_2}\left<\begin{matrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{matrix}\right>\mathrm{C(CO_2Et){\cdot}C({:}NH){\cdot}CH(CN){\cdot}CO_2Et.}$$

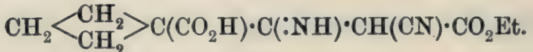
(I.)

The hydrolysis had evidently therefore taken place in accordance with the equation:



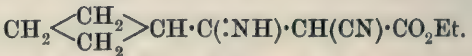
$$\mathrm{CH_2}{<}\substack{\mathrm{CH_2}\\ \mathrm{CH_2}}{>}\mathrm{C(CO_2Et)\cdot C(\colon NH)\cdot CH(CN)\cdot CO_2Et} \longrightarrow \mathrm{CH_2}{<}\substack{\mathrm{CH_2}\\ \mathrm{CH_2}}{>}\mathrm{C(CO_2H)_2} + \mathrm{CH_2(CO_2H)_2} + \text{etc.}$$

The constitution of the imino-compound was further shown by the products formed from it on partial hydrolysis. Thus, with dilute alkali hydroxide, it yields the alkali salt of *ethyl β-imino-α-cyano-1-carboxy-β-*cyclo*butyl-1-propionate*, from which the free ethyl hydrogen salt (II) can be prepared by the action of acids. This substance exists in two well-defined modifications, which melt at 75° and 156° respectively. We have named these compounds the α- and β-forms of the ethyl hydrogen salt, as we have been unable to determine their structural relationship:



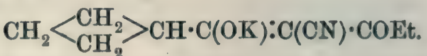
$$\mathrm{CH_2}{<}\substack{\mathrm{CH_2}\\ \mathrm{CH_2}}{>}\mathrm{C(CO_2H)\cdot C(\colon NH)\cdot CH(CN)\cdot CO_2Et.}$$

(II.)



$$\mathrm{CH_2}{<}\substack{\mathrm{CH_2}\\ \mathrm{CH_2}}{>}\mathrm{CH\cdot C(\colon NH)\cdot CH(CN)\cdot CO_2Et.}$$

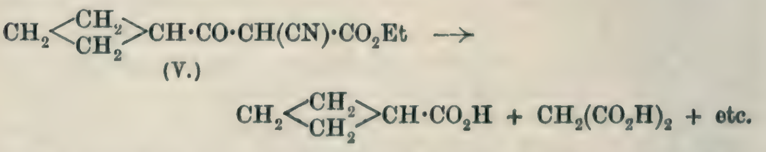
(III.)



$$\mathrm{CH_2}{<}\substack{\mathrm{CH_2}\\ \mathrm{CH_2}}{>}\mathrm{CH\cdot C(OK)\colon C(CN)\cdot COEt.}$$

(IV.)

Both modifications lose carbon dioxide when heated, and pass into *ethyl β-imino-α-cyano-β-*cyclo*butylpropionate* (III), a tautomeric amino-imino-compound, which, when treated with potassium hydroxide, passes into the stable *potassium* salt (IV). When a solution of this potassium salt is acidified, *ethyl α-cyano-β-*cyclo*butylformylacetate* (V) is precipitated, and from this compound *cyclo*butanecarboxylic acid and malonic acid can be prepared by hydrolysis:



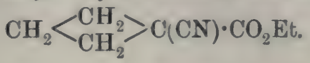
$$\mathrm{CH_2}{<}\substack{\mathrm{CH_2}\\ \mathrm{CH_2}}{>}\mathrm{CH\cdot CO\cdot CH(CN)\cdot CO_2Et} \longrightarrow \mathrm{CH_2}{<}\substack{\mathrm{CH_2}\\ \mathrm{CH_2}}{>}\mathrm{CH\cdot CO_2H} + \mathrm{CH_2(CO_2H)_2} + \text{etc.}$$

(V.)

The experiments recorded are of interest as showing the relative stability of the *cyclo*propane and *cyclo*butane rings under precisely similar conditions. The subject has been fully discussed by Perkin and Simonsen in two recent papers (Trans., 1907, **91**, 816; 1909, **95**, 1166), and as our knowledge of these compounds increases, it becomes evident that any generalisation respecting the stability and ease of formation of the alicyclic systems must take into account not merely the formation of the rings as such, but also the influence exerted by the groups substituting the carbon atoms composing the rings. We have at the present time a series of experiments in progress which it is hoped will throw further light on this question.

EXPERIMENTAL.

Ethyl 1-*Cyano*cyclo*butane*-1-*carboxylate*,



$$CH_2{<}{}^{CH_2}_{CH_2}{>}C(CN)\cdot CO_2Et.$$

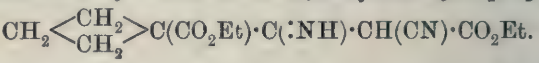
This substance was originally prepared by Carpenter and Perkin by the action of bromo*cyclo*butane on the sodium compound of ethyl cyanoacetate (Trans., 1899, **75**, 930). The compound prepared by them gave, however, figures on analysis ($C=58{\cdot}59$; $H=7{\cdot}04$. $C_8H_{11}O_2N$ requires $C=62{\cdot}7$; $H=7{\cdot}2$ per cent.) which clearly showed, as they remarked, that it must have contained nearly 50 per cent. of ethyl cyanoacetate. We have prepared a quantity of this mixture in the manner described by Carpenter and Perkin, and find that it is quite impossible, even by repeated fractionation, to separate the cyclic ester from ethyl cyanoacetate, which always accompanies it. Recently (this vol., p. 1002), we had occasion to prepare pure ethyl 1-cyano*cyclo*propane-1-carboxylate, and found that it could be separated from ethyl cyanoacetate by adding the calculated quantity of sodium ethoxide to the mixture to form the sodium derivative of ethyl cyanoacetate, and then by adding water to form the soluble sodium salt of cyanoacetic acid, leaving the pure cyclic ester undissolved.

We have now applied this method successfully for the preparation of pure ethyl 1-cyano*cyclo*butane-1-carboxylate in the following way. The mixed esters prepared by Carpenter and Perkin's method were fractionally distilled, and the fraction boiling at 214° was analysed. (Found, $C=59{\cdot}21$. $C_8H_{11}O_2N$ requires $C=62{\cdot}7$. $C_5H_7O_2N$ requires $C=53{\cdot}1$ per cent.) The mixture therefore contained approximately 37 per cent. of ethyl cyanoacetate. One hundred grams were therefore added to a well-cooled solution of 7·6 grams of sodium in 100 grams of alcohol, and the product was diluted with water. The oil which then separated was extracted by ether, and the residue left after evaporating the dried ethereal solution was distilled. Pure *ethyl* 1-*cyano*cyclo*butane*-1-*carboxylate* is a clear, colourless liquid, boiling at 218°/762 mm.:

0·2119 gave 0·4856 CO_2 and 0·1392 H_2O. $C=62{\cdot}51$; $H=7{\cdot}3$.

$C_8H_{11}O_2N$ requires $C=62{\cdot}7$; $H=7{\cdot}2$ per cent.

*Ethyl β-Imino-α-cyano-*1-*carbethoxy-β-*cyclo*butyl-*1-*propionate,*



$$CH_2<\substack{CH_2\\CH_2}>C(CO_2Et)\cdot C(:NH)\cdot CH(CN)\cdot CO_2Et.$$

This substance was prepared by the condensation of ethyl sodiocyanoacetate with ethyl 1-cyano*cyclo*butane-1-carboxylate in the following manner. 2·3 Grams of sodium were dissolved in 30 grams of alcohol, and the solution, after being mixed with 11·3 grams of ethyl cyanoacetate, was treated with 15·3 grams of ethyl 1-cyano-*cyclo*butane-1-carboxylate, and the whole heated on the water-bath for three hours. At the end of this time the dark-coloured, gelatinous product was mixed with water, and after the solution had been rendered faintly acid by acetic acid, it was distilled in a current of steam until the distillate was free from oil. The non-volatile residue, which solidified on cooling, was collected and crystallised from alcohol, from which solvent it separated in small, rectangular plates, melting at 111°:

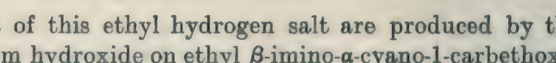
0·1861 gave 0·4007 CO_2 and 0·1151 H_2O. C = 58·7; H = 6·87.
0·2012 ,, 18·0 c.c. N_2 at 9° and 757 mm. N = 10·7.
$C_{13}H_{18}O_4N_2$ requires C = 58·6; H = 6·8; N = 10·5 per cent.

If the mixture of ethyl 1-cyano*cyclo*butane-1-carboxylate and ethyl cyanoacetate is used in this experiment instead of the pure cyclic ester, the product always consists of the above cyclic imino-compound mixed with ethyl β-imino-α-cyanoglutarate,

$$CO_2Et\cdot CH_2\cdot C(:NH)\cdot CH(CN)\cdot CO_2Et,$$

which has been formed by the condensation of ethyl cyanoacetate with its sodium derivative. The mixture may be separated by means of boiling sodium carbonate solution, which hydrolyses ethyl β-imino-α-cyanoglutarate to the sodium salt of ethyl hydrogen β-imino-α-cyanoglutarate, and leaves the cyclic imino-compound unchanged.

*The α- and β-forms of Ethyl β-Imino-α-cyano-*1-*carboxy-β-*cyclo*butyl-*1-*propionate,*



$$CH_2<\substack{CH_2\\CH_2}>CH(CO_2H)\cdot C(:NH)\cdot CH(CN)\cdot CO_2Et.$$

The two forms of this ethyl hydrogen salt are produced by the action of potassium hydroxide on ethyl β-imino-α-cyano-1-carbethoxy-β-*cyclo*butyl-1-propionate, the α-form at low temperatures, the β-form when the reaction is carried out at the temperature of boiling water. The conditions found most suitable for their production were as follows.

α-Form. — Ethyl β-imino-α-cyano-1-carbethoxy-β-*cyclo*butyl-1-propionate slowly dissolves when shaken with a solution containing rather more than the calculated quantity of potassium hydroxide dissolved in three times its weight of water, and if, when all has passed into solution, hydrochloric acid is cautiously added until an acid reaction is obtained, an oil separates which solidifies on being scratched. When crystallised from warm water, this form of the ethyl hydrogen salt is obtained in colourless needles, which melt at 75°, and lose carbon dioxide at a higher temperature:

0·1798 gave 0·3633 CO_2 and 0·0927 H_2O. C = 55·1; H = 5·72.

$C_{11}H_{14}O_4N_2$ requires C = 55·4; H = 5·8 per cent.

The *α*-form is very unstable, and readily gives off carbon dioxide; even when an aqueous solution of it is boiled, considerable decomposition ensues.

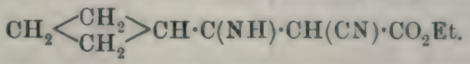
β-Form.—Some of this modification always accompanies the *α*-form, and can be obtained from the mother liquors employed in its recrystallisation. It can be prepared as chief product by using the following conditions. Ethyl *β*-imino-*α*-cyano-1-carbethoxy-*β*-*cyclo*butyl-1-propionate is suspended in boiling water, and rather more than the calculated quantity of aqueous potassium hydroxide added to the hot liquid. The ester quickly dissolves, and the solution is then cooled and acidified, when crystals separate at once. When recrystallised from hot water, the small prisms of the *β*-form are obtained, which melt and evolve carbon dioxide at 156°:

0·1790 gave 0·3649 CO_2 and 0·0937 H_2O. C = 55·6; H = 5·8.

$C_{11}H_{14}O_4N_2$ requires C = 55·4; H = 5·8 per cent.

The *β*-form of the ethyl hydrogen salt is very stable, and can be boiled with water for a considerable time without undergoing change. The alkali salt of the *α*-form is completely transformed into the alkali salt of the *β*-modification when its aqueous solution is boiled, but the reverse change could not be effected.

*Ethyl β-Imino-α-cyano-β-*cyclo*butylpropionate,*



$$CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>CH\cdot C(NH)\cdot CH(CN)\cdot CO_2Et.$$

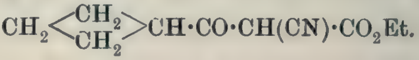
This substance is formed when either the *α*- or *β*-form of ethyl *β*-imino-*α*-cyano-1-carboxy-*β*-*cyclo*butyl-1-propionate is heated until the evolution of gas has ceased. The operation is conducted in a test-tube heated in a bath of sulphuric acid, and when all carbon dioxide has been evolved, the residue, which solidifies on cooling, is crystallised from dilute methyl alcohol. The imino-compound forms slender needles, which melt at 105°:

0·1821 gave 0·4125 CO_2 and 0·1203 H_2O. C = 61·78; H = 7·34.

$C_{10}H_{14}O_2N_2$ requires C = 61·9; H = 7·2 per cent.

*Ethyl β-imino-α-cyano-β-*cyclo*butylpropionate* is a tautomeric imino-amino(ketimino-enamic)-derivative, which is slowly hydrolysed by dilute mineral acid to the corresponding ketone. It is also readily hydrolysed by aqueous alkali hydroxides, forming the stable alkali salt of the enolic form of the ketone.

*Ethyl α-Cyano-β-*cyclo*butylformylacetate,*



$$\mathrm{CH_2}{<}\substack{\mathrm{CH_2}\\ \mathrm{CH_2}}{>}\mathrm{CH\cdot CO\cdot CH(CN)\cdot CO_2Et.}$$

This substance can be prepared by the action of dilute sulphuric acid on the last-named imino-compound, but is more conveniently produced by the action of aqueous potassium hydroxide. Five grams of the imino-compound are mixed with water, and slightly more than the calculated quantity of aqueous potassium hydroxide is added. The imino-compound rapidly dissolves when the solution is warmed, ammonia being evolved at the same time, and if, when all has passed into solution, it is rendered acid by hydrochloric acid, an oil is precipitated which can be extracted by ether. It is advisable, in order further to purify the ketone, to shake the ethereal solution with aqueous sodium carbonate, and then to recover the ketone by acidifying the alkaline extract and extracting it again with ether. *Ethyl α-cyano-β-*cyclo*butylformylacetate* is a colourless oil, which boils at 182°/25 mm.:

0·2077 gave 0·4676 CO_2 and 0·1270 H_2O. C = 61·41; H = 6·8.

$C_{10}H_{13}O_3N$ requires C = 61·5; H = 6·7 per cent.

The ester dissolves readily in aqueous alkali hydroxides and in solutions of alkaline carbonates. It gives an intense red coloration in alcoholic solution with ferric chloride.

The *silver* salt separates as a microcrystalline precipitate when the calculated quantity of silver nitrate solution is added to a neutral solution of the ammonium salt of the ketone:

0·2973 gave 0·1062 Ag. Ag = 35·72.

$C_{10}H_{12}O_3NAg$ requires Ag = 35·76 per cent.

The salt rapidly becomes coloured on exposure to light.

Formation of cyclo*Butane-*1 : 1*-dicarboxylic Acid and Malonic Acid from Ethyl β-Imino-α-cyano-*1*-carbethoxy-β-*cyclo*butyl-*1*-propionate.*

This decomposition was effected by boiling 7 grams of the imino-compound with 20 per cent. sulphuric acid for four hours; the resulting clear solution was then distilled in a current of steam until the odour of *cyclo*butanecarboxylic acid, which resembles that of *iso*butyric acid, ceased to be apparent, and the distillate showed a neutral reaction. The non-volatile residue was then saturated with ammonium sulphate, and extracted repeatedly with ether. The dried ethereal extract, on evaporation, left a residue which solidified. This was found to consist of a mixture of *cyclo*butane-1 : 1-dicarboxylic acid and malonic acid, and was separated by treatment with concentrated hydrochloric acid, in which the cyclic acid is insoluble. The pure acid was obtained in prisms, melting and decomposing at 155°. (Found, C=49·98; H=5·73. Calc., C=50·0; H=5·5 per cent.)

Malonic acid was recovered from the mother liquors used in the separation of the above acid by evaporating them to dryness and extracting the residue with ether. It was characterised by its conversion into acetic acid on distillation.

Formation of cyclo*Butanecarboxylic Acid and Malonic Acid from Ethyl α-Cyano-β-*cyclo*butylformylacetate.*

Some *cyclo*butanecarboxylic acid is formed in the hydrolysis just described, and can be recovered from the steam distillate. The quantity is, however, very small, being only about 3 per cent. of the amount of imino-compound hydrolysed. The cyclic acid can, however, be prepared in quantitative yield from ethyl α-cyano-β-*cyclo*butylformylacetate in the following manner. Ten grams are boiled with 20 per cent. sulphuric acid for four hours, when the acid solution is distilled in a current of steam until the distillate ceases to be acid. The distillate is then saturated with ammonium sulphate and extracted with ether. The dried ethereal extract leaves a residue on evaporation which distils at 191°, and possesses a characteristic odour resembling that of *iso*butyric acid. The acid was converted into its silver salt, which crystallises from hot water in long needles. (Found, Ag=52·3. Calc., Ag=52·2 per cent.)

The non-volatile portion from the steam distillate was saturated with ammonium sulphate and extracted with ether. The residue, on evaporating the ether, melted at 132°, and was proved to be malonic acid by converting it into acetic acid by distillation.

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CCXLIX.—*The Wet Oxidation of Metals. Part I. The Rusting of Iron.*

By Bertram Lambert (Goldsmiths' Research Student) and James Campbell Thomson.

The work of Moody (Trans., 1906, **89**, 720) and Friend (Proc., 1910, **26**, 179) would seem to point to the fact that ordinary "commercial" iron can, in some circumstances, be kept for a considerable time without undergoing visible oxidation in contact with water and air freed from acid gases, such as carbon dioxide.

These experiments are perhaps generally accepted as strong evidence in support of an explanation of the rusting of iron which was originally put forward by Crum Brown in 1888. His theory is that the rusting of iron is due primarily to the interaction between iron, carbon dioxide, and water, with the formation of ferrous bicarbonate, which then reacts with oxygen to form ferric oxide.

The impurities contained in the best commercial iron must, from a chemical point of view, be regarded as considerable, and, in the light of our present knowledge of the great modifications capable of being produced in the properties of substances by the presence of even minute traces of impurities, it cannot be contended that experiments with impure iron afford trustworthy grounds for a satisfactory theory of the oxidation of iron.

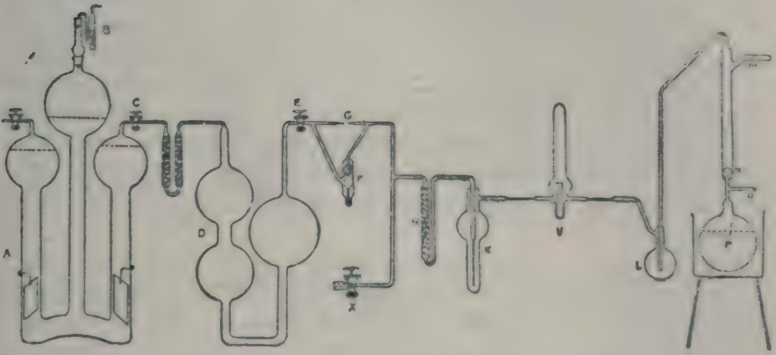
The aim of the present investigation was to bring together, under the simplest possible conditions, the purest obtainable water, oxygen, and iron, in vessels which would be least likely to be acted on by any of these substances.

The results have been to show that chemically pure iron will not undergo visible oxidation even after long exposure to pure water and pure oxygen in vessels made of clear fused silica. Further, that a very small trace of impurity in the iron is sufficient to cause oxidation under exactly the same conditions, where there is not the remotest chance of any acid substance either being present or being formed during the reaction.

Description of Apparatus: Preparation of Oxygen and Water.

Oxygen.—The oxygen used in the experiments was prepared by the electrolysis of a solution of barium hydroxide in "conductivity" water. The barium hydroxide was purified by recrystallising twelve times. The solution was electrolysed between platinum plates in a cell *A* (Fig. 1), the air entering the reservoir of the cell, owing to changes of pressure during the electrolysis, being purified by passing through tubes containing sulphuric acid and soda-lime, as shown at *B*. The oxygen was stored in a series of flasks, *D*, of about 2 litres capacity. Before reaching the storage vessels, the oxygen was passed through a U-tube containing lumps of pure sodium hydroxide to remove the excess of aqueous vapour. This was found necessary in order to protect the lubrication of phosphoric acid on the tap *E*, which connected the oxygen storage with the rest of the apparatus. Even with this precaution, it was found that there was a slight leakage round this tap when there was a high vacuum in the rest of the apparatus. This was prevented by introducing a mercury trap of the type shown in the figure at *F*. (The principle of this trap is explained later.)

FIG. 1.



All the taps were mercury-sealed and lubricated with glacial phosphoric acid.

Water.—The water was prepared by distillation, in a vacuum, from a concentrated solution of barium hydroxide. The barium hydroxide, purified as before, was dissolved in "conductivity" water in the flask *P*, which was separated from the rest of the apparatus by a thin bulb, *N*, sealed into a wider tube connecting with the rest of the apparatus, as shown in the figure. Connexion was made between the water supply and the rest of the apparatus, at the proper time, by causing the glass rod at *M* to drop on the thin bulb *N* and break it.

The air in contact with the baryta solution was removed through the side-tube *O*, which was drawn out to a capillary and attached to a good water-pump. The water in the flask was then boiled vigorously, under diminished pressure, for two or three hours, the capillary being sealed while the water was boiling. In this way all but the smallest traces of air were removed from the flask.

The "conductivity" water used to prepare the solutions of barium hydroxide for the cell *A* and the flask *P* was made by Kohlrausch's method by distillation through alkaline and acid solutions of potassium permanganate. It was condensed in a block-tin condenser, and collected and stored in a large Jena-glass flask, with arrangements for syphoning off and for protecting it from contact with impure air, as used by Hartley, Campbell, and Poole (Trans., 1908, **93**, 428). Only the middle portions of the distillate were used. This water was also used in the final washing of all parts of the apparatus before they were set up.

The choice of the kind of vessel in which to carry out the experiments was the cause of much difficulty. It was finally decided to use vessels made of transparent fused silica as being least likely to be affected by either water, iron, or oxygen. After many trials and experiments, a simple form of glass vessel was devised, which, with a tube of clear fused silica, gave all the advantages of an apparatus made entirely of silica, since the water which collected in the silica tube and came in contact with the iron must have condensed on the inside of the silica tube itself. The silica tubes were about 8 cm. in length and 1 cm. in diameter, and were closed at one end.

A silica tube was made to slide loosely into an outer glass vessel, of the shape shown at *V* in the figure, and to be so supported by the lower end of the glass vessel that the open end of the tube and half its length were not in contact with the glass. The pure iron (preparation described later) was put into the silica tube, which was then placed in the outer glass vessel; the glass vessel was then closed at the top and sealed into position by means of the side-tubes connecting with the oxygen supply and the water supply, as shown in the figure. These side-tubes were drawn out to capillaries in order to facilitate the sealing off of the vessel when the experiment was finished. (Three or four such vessels were used in each experiment, and were sealed on in parallel.)

Between the vessel *V* and the water supply was a trap *L*, to catch and retain any water which condensed before reaching this point. Between the vessel *V* and the oxygen supply was a trap *K*, of shape shown in the figure, the use of which is explained below, and a tube *H*, containing glass-beads covered with pure gold-leaf. This device was used to protect the vessel containing the iron from contamination with mercury vapour, for, in evacuating the apparatus, a very high vacuum was obtained, and mercury was contained both in the trap *F* and in the pumps.

All joints in the apparatus were sealed glass joints, and no rubber connexions of any kind were used.

All the glass parts of the apparatus were very thoroughly cleaned and steamed, at intervals, for several hours.

The silica tubes were boiled with pure concentrated nitric acid for several weeks, and were afterwards steamed and boiled with constant changes of freshly made conductivity water for several days. They were finally heated strongly in a clear blow-pipe flame.

The whole apparatus was connected, beyond the tap *X*, with a combined Sprengel and Töpler pump and a drying tube containing phosphoric oxide.

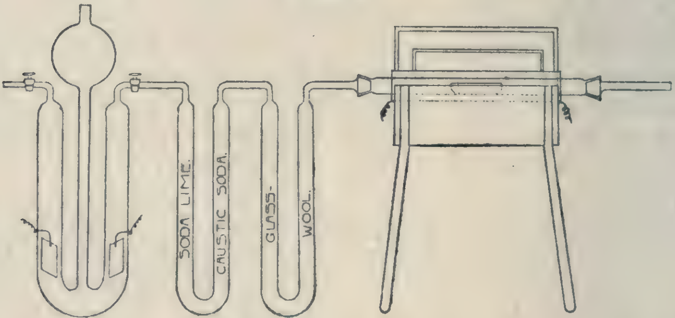
Method of Conducting the Experiment.—The whole apparatus between the bulb *N* (separating the water supply) and the tap *C* was evacuated. The tap *E* was then closed, and the storage vessels *D* filled with oxygen made by electrolysis of the baryta in the cell *A*. The capillary at *G* was sealed, so that any slight leakage of oxygen round the tap *E* merely served to push up the mercury in the trap *F*, and did not affect the vacuum in the rest of the apparatus. The thin bulb *N* was then broken by causing the heavy glass rod *M* to fall on it. It was usually found that there was a little residual air in the flask *P*, which had not been completely removed in the boiling off process. The quantity of air was extremely small, and was easily removed by working the mercury pumps for a few minutes.

The flask *P* was then very gently heated on a water-bath, the temperature never being raised so high as to promote rapid evaporation. The first portions of water were caused to condense in the vessel *K* by surrounding it with ice. When the water collected in *K* reached a depth of about 12 cm., the lower end of the vessel *V* was cooled, and water slowly condensed inside the silica tube and in contact with the iron. The water collecting in the silica tube must necessarily have condensed only on silica; any water which condensed on the glass vessel supporting the silica tube simply running down and collecting outside the silica tube.

When a sufficient quantity of water had been obtained in contact with the iron, the capillary to the right of *V* was sealed off by means of a small flame. Oxygen was then allowed to enter the apparatus by slowly opening the tap *E*. This pure oxygen, before entering *V*, was washed by passing through the pure water collected in the trap *K* for this purpose. The capillary to the left of *V* was then sealed, thus leaving the iron in contact with pure water and pure oxygen in a sealed vessel. The vessel was put aside for observation.

Preparation of Pure Iron.—The material employed in the preparation of pure iron was a pure specimen of "Kahlbaum" ferric chloride. The salt was found to be free from sulphate, arsenic, alkali, or alkaline earth metals. A solution of the salt was made in conductivity water and electrolysed between electrodes of pure iridium foil. This method is made possible by the fact that pure iridium is not attacked by chlorine, which is evolved at the anode. The metallic iron which was deposited on the cathode was then thoroughly washed with conductivity water, and dissolved in pure dilute nitric acid. This solution of ferric nitrate in excess of nitric acid was concentrated on the water-bath, and the salt crystallised from the solution in concentrated nitric acid. The crystals were separated from the mother liquor, washed with pure concentrated nitric acid, and recrystallised four or five times from this solvent. The crystals so obtained were colourless, or white when seen in bulk. It is to be noticed that ferric nitrate, prepared from ordinary pure iron, has, when seen in bulk, a pale violet colour like that of iron alum, and that the colour cannot be removed by repeated crystallisation from pure nitric acid.

Fig. 2.



The ferric nitrate crystals were transferred by means of a spatula of iridium foil to a pure iridium boat. The boat was then heated in air on a thick tile, so that the flame gases did not come in contact with it. The ferric nitrate was thus converted into the oxide or basic nitrate. The boat containing the flakes of oxide was then placed into a transparent silica tube, and heated in an electric resistance furnace to a bright red heat (just above 1000°), while a stream of pure hydrogen was passed through the tube.* Fig. 2

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* In some experiments the oxide was heated in a stream of pure oxygen for several hours before being reduced, in order to remove the occluded nitrogen which is contained in most oxides formed from nitrates. This operation, however, was found to be unnecessary, since the properties of the resulting iron were exactly the same as when the oxide or basic nitrate was directly reduced in hydrogen. The

shows the arrangement of the apparatus for this operation. The hydrogen was prepared by the electrolysis of a solution of pure barium hydroxide. The figure only shows half the electrolytic cell, which contains two pairs of large platinum electrodes and is capable of producing a steady stream of hydrogen. The gas was passed through a U-tube containing lumps of pure sodium hydroxide, in order to remove excess of water vapour, and then through another U-tube containing tightly-packed glass wool.

The metallic iron so obtained, by direct reduction of the flakes of oxide or basic nitrate, had a distinct metallic lustre and a light grey colour. If the flakes of oxide were ground in an agate mortar before being reduced, the iron produced by reduction was light grey in colour, but had little or no lustre. The properties of the two kinds of iron were the same.

The Jena-glass beakers used in the preparation of the ferric nitrate were thoroughly cleaned and boiled out for several weeks with constant changes of pure concentrated nitric acid. They were also steamed out at intervals for several hours. The same treatment was applied to a Gooch crucible, which was used for separating and washing the ferric nitrate crystals. The iridium boat was boiled for several weeks with aqua regia and then with concentrated nitric acid; it was finally heated to a high temperature in a stream of hydrogen in the electric resistance furnace.

The nitric acid used throughout in the preparation of ferric nitrate was made by the distillation, under diminished pressure, of a pure commercial nitric acid. The acid was distilled twice, the first and last portions of the distillate being discarded in both cases.

Fig. 3 shows the apparatus which was used for the distillation of the nitric acid. The acid was introduced into the distilling flask *A* by means of the side-tube *B*, which was then sealed off. The connexions between distilling flask, condenser, and receiver were sealed joints. Nitric acid distilled under low pressure is very liable to froth violently, and so a large trap was introduced at *C*. A good water-pump was used to evacuate the apparatus through the tap *D*. The acid was drawn off through the tube *E* by cutting off a small portion of the capillary, which was sealed up again immediately afterwards. After this apparatus had been used for several weeks and the surface alkali had been dissolved from the glass, the nitric acid obtained was very pure, and 50 c.c. left no weighable residue when evaporated to dryness on the water-bath. The product

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slight surface oxidation undergone by the iridium did not seem to affect the iron. The occluded nitrogen was undoubtedly removed by heating in hydrogen to the high temperature of the furnace. This temperature was between the melting point of silver and that of copper.

obtained by distilling nitric acid from a platinum retort was not nearly so good.

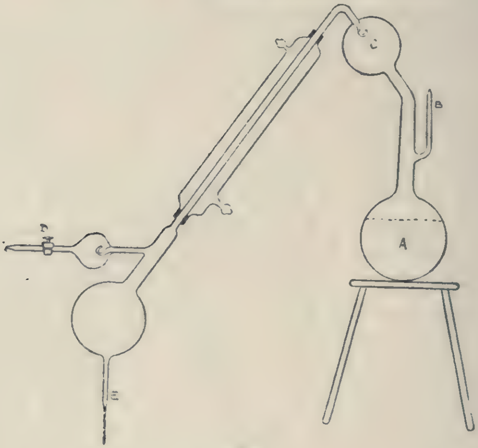
It is to be noticed that throughout the preparation of pure iron the use of platinum apparatus was avoided.

Results of Experiment and Conclusions.

It was found that pure iron, prepared exactly as described above, did not undergo any visible oxidation when treated with pure water and pure oxygen in vessels made of clear fused silica, and that there was no change even after several months.

If, however, ferric nitrate, prepared from ordinary pure iron, was used, even after ten recrystallisations, and iron made from it by precisely the same method, the iron invariably showed signs of oxidation in two or three hours, and, after twelve hours, there was always a considerable deposit of reddish-yellow ferric oxide on parts of the metal. Oxidation also took place even when the oxide prepared from the nitrate was strongly heated in a stream of pure oxygen for several hours before being reduced to the metal.

Fig. 3.



It is impossible that iron prepared in this way can contain anything more than a very slight trace of impurity, and that impurity, whatever it may be, cannot be of such a nature that it is acid, or will give an acid on oxidation.

Again, if platinum vessels were used, particularly if a platinum boat was used in which to reduce the iron, the iron produced readily underwent oxidation in two or three hours, and oxidation invariably took place at those parts of the metal which had been heated in contact with the platinum boat.

Richards (*Proc. Amer. Acad.*, 1900, **35**, 253), in his work on the atomic weight of iron, prepared iron in somewhat the same way as we have done, but he distilled the nitric acid used from a platinum retort, and employed platinum vessels throughout for his preparation. He states that the iron always contained slight traces of platinum, and that, when it was dissolved in acids, a small black speck of platinum remained.

This small trace of platinum, which may be merely attached to the iron, or may be present in the form of a solid solution, would seem to be enough to cause oxidation to take place.

All kinds of commercial iron which were used readily rusted under the same conditions of experiment, as also did iron made with the most scrupulous care by many other methods.

A specimen of commercial electrolytic sheet iron (99·9 per cent. of iron), which had been polished and treated with a 1 per cent. solution of chromic acid for three months, and afterwards washed with pure water and quickly dried, readily rusted under the same conditions of experiment. This method of treating ordinary iron is said by Moody to remove the impurities from the surface of the iron. It seems probable that other reasons must be sought for the non-rusting of the commercial iron used by Moody under his precise conditions of experiment.

It would seem to be proved from these experiments that pure iron will not undergo visible oxidation in contact with pure water and pure oxygen, but that a small trace of impurity in the iron is sufficient to cause oxidation under exactly the same conditions of experiment, even if this impurity be not of an acid nature or likely to produce an acid during the reaction.

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CCL.—*Preparation of Secondary Amines from Carboxylic Acids. Part I. Preparation of Heptadecylaniline, Pentadecylaniline, and Tridecylaniline.*

By HENRY RONDEL LE SUEUR.

THE method most generally employed for the preparation of secondary amines consists in the interaction of an alkyl haloid compound and a primary amine. A serious objection to this method is that tertiary amines are also formed, and the subsequent separation of the secondary amines from these is a matter of considerable difficulty. Further, this method necessitates the use of alkyl monohaloid compounds, and these, with the exception of the lower members, are not always easy to prepare.

The method which is now brought forward for the preparation of monoalkylanilines, and which, so far as can be ascertained, is new, is free from these two objections, as, firstly, owing to the nature of the reaction, there is no possibility of the formation of dialkylanilines, and, secondly, the entering alkyl group results directly from an acid, and acids are more easily obtained than any other class of organic compounds. The new method is briefly as follows: (1) the α-anilino-acid is prepared by the interaction of aniline and the α-bromo-acid, (2) the α-anilino-acid is heated to considerably above its melting point, whereby it loses carbon dioxide, and a monoalkylaniline results:

$$\underset{\alpha\text{-Bromostearic acid.}}{CH_3\cdot[CH_2]_{15}\cdot CHBr\cdot CO_2H} + C_6H_5\cdot NH_2 = \underset{\alpha\text{-Anilinostearic acid.}}{CH_3\cdot[CH_2]_{15}\cdot CH(NHPh)\cdot CO_2H} + HBr.$$

$$CH_3\cdot[CH_2]_{15}\cdot CH(NHPh)\cdot CO_2H \xrightarrow{\text{heated}} \underset{\text{Heptadecylaniline.}}{CH_3\cdot[CH_2]_{15}\cdot CH_2\cdot NHPh} + CO_2.$$

In the three cases so far investigated, and which form the subject of this communication, the yield of α-anilino-acid was more than 70 per cent. of the theoretical, and the yield of alkylaniline was also more than 70 per cent. of that theoretically obtainable from the anilino-acid.

α-Anilinostearic acid, α-anilinopalmitic acid, and α-anilinomyristic acid have been already prepared by Hell and his collaborators (*Ber.*, 1889, **22**, 1748; 1891, **24**, 942, 2395), who obtained these compounds by the interaction of aniline and the respective α-bromo-acid at 180—185°. Heating to 180—185° is not necessary, and is to be avoided, as at this high temperature there is a likelihood of the anilino-acid undergoing decomposition, and also of the formation of an anilide and of an αβ-unsaturated acid, the latter being formed by the removal of hydrogen bromide from the α-bromo-acid by the aniline. *Heptadecylaniline*, $C_{17}H_{35}\cdot NH\cdot C_6H_5$, *pentadecylaniline*, $C_{15}H_{31}\cdot NH\cdot C_6H_5$, and *tridecylaniline*, $C_{13}H_{27}\cdot NH\cdot C_6H_5$, are colourless solids, which melt at a low temperature, and are readily soluble in most of the common organic solvents. Their hydrochlorides are insoluble in cold water, and when heated with this liquid they melt and undergo almost complete hydrolysis into the free base and hydrogen chloride.

The author is now engaged in the investigation of the application of the above reaction to the preparation of secondary amines in general, and more particularly of monoalkylnaphthylamines and other monoalkylanilines, and from the results so far obtained it is evident that this method is not limited to the preparation of the higher monoalkylanilines.

EXPERIMENTAL.

Preparation of α-Anilinostearic Acid, $C_{16}H_{33}\cdot CH(NHPh)\cdot CO_2H$.

Thirty grams of α-bromostearic acid (1 mol.) and an equal weight of aniline (4 mols.) were heated together in a flask immersed in boiling water for thirteen hours. The resulting solid was thoroughly digested with excess of hot dilute hydrochloric acid, collected, and washed with dilute acid and water to remove excess of aniline; it was then dried and crystallised from a mixture of alcohol and ethyl acetate, when 23 grams of the pure acid were obtained. (Found, C = 76·54; H = 10·75; N = 3·91. Calc., C = 76·80; H = 10·93; N = 3·73 per cent.)

α-Anilinostearic acid is sparingly soluble in alcohol, acetone, benzene, or chloroform in the cold, but dissolves readily on heating. It is insoluble in water, ether, or light petroleum, and separates from ethyl acetate in nodular aggregates, melting at 141—142°, and not at 84·5°, as stated by Hell and Sadomsky (*Ber.*, 1891, **24**, 2395). The low melting point given by Hell and Sadomsky is obviously not in agreement with the value to be expected from analogy to other similar α-anilino-acids.

Heptadecylaniline, $C_{17}H_{35}\cdot NH\cdot C_6H_5$.

Five grams of α-anilinostearic acid were placed in a small flask containing a thermometer, the bulb of which dipped into the substance, and the whole heated in a metal-bath. As soon as the substance was melted, the temperature was raised rapidly to about 190°, at which point the evolution of carbon dioxide commenced. The temperature was then raised more slowly to 270—280°, and the heating stopped when the evolution of carbon dioxide had ceased. The evolution of carbon dioxide is very rapid at about 220°, and there is no evidence of charring or secondary decomposition at any stage of the heating, which for 5 grams of acid requires about fifteen minutes. The product resulting from 20 grams of anilino-acid, heated in quantities of 5 grams at one time as described above, was distilled under 50 mm. pressure, when 14·3 grams of distillate, boiling between 295° and 300°, were obtained. This was redistilled under 35 mm. pressure, and gave:

Below 285°	2·3 grams.
285—290°	10·0 ,,

Undistilled residue = 2·0 grams.

The fraction 285—290° readily solidified to a white solid melting at 41—42°, and consisted therefore of the pure amine, and, as nearly the whole of the fraction distilled at 285—286°, this temperature is to be regarded as the boiling point of the pure substance. The amine was also purified by crystallisation instead of fractional distillation, in which case the method adopted was as follows. The product resulting from the heating of the anilino-acid was distilled in a vacuum and the distillate dissolved in ether, the ethereal solution washed with a solution of potassium hydroxide, dried with solid potassium hydroxide, and the residue left on evaporation of the ether crystallised from alcohol until its melting point was constant. This alternative method of purification is especially applicable to the preparation of small quantities of the amine:

0·1632 gave 0·5000 CO_2 and 0·1836 H_2O. $C = 83·55$; $H = 12·50$.
0·2380 „ 8·7 c.c. N_2 (moist) at 12° and 770 mm. $N = 4·40$.
$C_{23}H_{41}N$ requires $C = 83·38$; $H = 12·38$; $N = 4·23$ per cent.

Heptadecylaniline is readily soluble in ether, benzene, chloroform, acetone, light petroleum, or ethyl acetate in the cold, sparingly so in cold alcohol, but readily so on warming, and crystallises from this solvent in large plates, which soon change to long needles, the latter being the stable crystalline form. Heptadecylaniline melts at 42—43°, and boils at 285—286°/35 mm. It is insoluble in hydrochloric acid, but dissolves readily in concentrated sulphuric acid.

The *hydrochloride*, $C_{17}H_{35}\cdot NH\cdot C_6H_5,HCl$, was obtained by dissolving 1·5 grams of the amine in 50 c.c. of ether, and passing dry hydrogen chloride into the solution until saturated. The precipitated hydrochloride was collected, washed with ether, dried, and crystallised from light petroleum (b. p. 60—80°), when it was obtained in beautiful, thin, glistening plates, melting at 99—100°. It is sparingly soluble in alcohol, ether, acetone, benzene, or light petroleum in the cold, and readily dissolves in cold chloroform or boiling light petroleum. It is insoluble in cold water; in hot water, however, the substance melts, but does not dissolve, and the aqueous liquid acquires a strongly acid reaction. 0·2856 Gram, suspended in hot water, required 7·8 c.c. $N/10$-NaOH for neutralisation of the aqueous solution, using methyl-orange as indicator, whereas the same weight of the compound, $C_{17}H_{35}\cdot NH\cdot C_6H_5,HCl$, requires 7·8 c.c. $N/10$-NaOH.

The *acetyl* derivative, $C_{17}H_{35}\cdot N(CH_3\cdot CO)\cdot C_6H_5$, was readily prepared by boiling together half a gram of the amine and two grams of acetic anhydride for one and a-half hours. The excess of acetic anhydride was removed by allowing the product to remain in a vacuum over a saturated solution of potassium hydroxide, and the solid residue was purified by crystallisation from methyl alcohol containing a small quantity of water:

0·1690 gave 5·9 c.c. N_2 (moist) at 20° and 750 mm. N = 3·94.

$C_{25}H_{43}ON$ requires N = 3·75 per cent.

Acetoheptadecylanilide is readily soluble in most of the ordinary organic solvents, and crystallises from methyl alcohol containing a little water in feathery aggregates of slender needles, melting at 42—43°.

The *nitrosoamine*, $C_{17}H_{35}\cdot N(NO)\cdot C_6H_5$, was most easily obtained by the following method, which gave a practically theoretical yield of the pure substance. 1·5 Grams of the amine were dissolved in 10 c.c. of concentrated sulphuric acid, and this solution added drop by drop to a solution of 3 grams of sodium nitrite in 80 c.c. of water, the whole being vigorously shaken, and more (about 2 grams) sodium nitrite added from time to time. The resulting solid was collected, washed, dried, and crystallised from methyl alcohol:

0·1520 gave 10·5 c.c. N_2 (moist) at 18·5° and 760 mm. N = 7·96.

$C_{23}H_{40}ON_2$ requires N = 7·78 per cent.

Phenylheptadecylnitrosoamine is readily soluble in ether, chloroform, benzene, light petroleum, or acetone in the cold, sparingly so in cold methyl alcohol, but dissolves readily on heating, and crystallises from this solvent in light fawn-coloured plates, melting at 53—54°. A small quantity of the nitrosoamine, mixed with a little phenol and warmed with concentrated sulphuric acid, gave a blue solution, which, on dilution, gave a red, opalescent liquid, turning blue on being rendered alkaline.

Preparation of α-Anilinopalmitic Acid.

Thirty grams (1 mol.) of α-bromopalmitic acid and an equal weight (3½ mols.) of aniline were heated together in a flask immersed in boiling water for seven hours, and the resulting product was worked up as described for the preparation of α-anilinostearic acid (p. 2435). The crude acid was purified by crystallisation from a mixture of alcohol and ethyl acetate, and was obtained in nodules, melting at 143—144°, a melting point which agrees with that given for this substance by Hell and Jordanoff (*Ber.*, 1891, **24**, 942). The yield of pure acid obtained corresponded with 80 per cent. of the theoretical. (Found, N = 4·09. Calc., N = 4·03 per cent.)

Pentadecylaniline, $C_{15}H_{31}\cdot NH\cdot C_6H_5$.

The α-anilinopalmitic acid was heated in quantities of 5 grams in a flask immersed in a metal-bath, as described for the preparation of heptadecylaniline (p. 2435). The evolution of carbon dioxide commenced at about 190°, was rapid at 220°, and had ceased after fifteen minutes' heating, the temperature having risen at the end of that time to 280°. The product resulting from 29 grams of anilino-acid heated as described above was distilled under 40 mm. pressure, when the following fractions were obtained:

Below 274°	2·8 grams.	290—340°	2·3 grams.
274—290°	17·7 ,,	Undistilled residue...	3·0 ,,

The fraction 274—290° was redistilled under 40 mm. pressure, when 16 grams, boiling at 271—274°, were obtained, which solidified to a colourless solid, melting at 32—33°, and consisted of the pure amine. The fraction boiling below 274° on crystallisation from alcohol gave 1·6 grams of the pure substance. The total weight of pure amine obtained from 29 grams of anilino-acid was 17·6 grams, which corresponds with a 70 per cent. yield of the theoretical:

0·1488 gave 0·4548 CO_2 and 0·1640 H_2O. C = 83·35; H = 12·24.

0·2164 ,, 8·8 c.c. N_2 (moist) at 18° and 762 mm. N = 4·71.

$C_{21}H_{37}N$ requires C = 83·17; H = 12·21; N = 4·62 per cent.

Pentadecylaniline is readily soluble in ether, benzene, chloroform, acetone, light petroleum, or ethyl acetate in the cold, is sparingly soluble in cold alcohol, but dissolves readily on warming, and crystallises from this solvent in feathery aggregates, melting at 34—35°. It is insoluble in hydrochloric acid, but dissolves readily in concentrated sulphuric acid. The pure amine boils at 271°/40 mm.

The *hydrochloride*, $C_{15}H_{31}\cdot NH\cdot C_6H_5,HCl$, was readily obtained by passing dry hydrogen chloride into a solution of 1 gram of pentadecylaniline in 30 c.c. of ether, when the pure hydrochloride soon crystallised in glistening plates, which melted at 97·5°. It is insoluble in ether, acetone, benzene, or light petroleum in the cold, dissolves readily in cold chloroform and in boiling light petroleum, from which it separates in glistening plates on cooling. It is insoluble in water, and when heated with this solvent it melts but does not dissolve, the water acquiring a strongly acid reaction.

0·2574 Gram, suspended in hot water, required 7·50 c.c. *N*/10-NaOH for neutralisation, using methyl-orange as indicator, whereas the same weight of the compound $C_{15}H_{31}\cdot NH\cdot C_6H_5,HCl$ requires 7·58 c.c. *N*/10-NaOH.

The *acetyl* derivative, $C_{15}H_{31}\cdot N(CH_3\cdot CO)\cdot C_6H_5$, was prepared by boiling 1 gram of the amine with 4 grams of acetic anhydride for four hours. The excess of anhydride was removed by allowing the product to remain in a vacuum over a concentrated solution of potassium hydroxide, and the residue crystallised from methyl alcohol containing a very little water:

0·2008 gave 7·5 c.c. N_2 (moist) at 27·5° and 766 mm. N = 4·14.
$C_{23}H_{39}ON$ requires N = 4·06 per cent.

Acetopentadecylanilide is very readily soluble in all the common organic solvents, and crystallises from methyl alcohol containing a little water in hair-like needles, melting at 30·5—31·5°.

The *nitrosoamine*, $C_{15}H_{31}\cdot N(NO)\cdot C_6H_5$, was prepared by adding a solution of 1 gram of the amine in 8 c.c. of concentrated sulphuric acid to a dilute solution of sodium nitrite, the latter being kept in considerable excess, as described for the preparation of the nitrosoamine of heptadecylaniline (p. 2437). The crude nitrosoamine was purified by crystallisation from methyl alcohol:

0·1420 gave 10·2 c.c. N_2 (moist) at 16° and 768 mm. N = 8·46.
$C_{21}H_{36}ON_2$ requires N = 8·43 per cent.

Phenylpentadecylnitrosoamine is readily soluble in ether, chloroform, light petroleum, acetone, or benzene in the cold, and crystallises from methyl alcohol in glistening, flat needles, which melt at 49°, and have a light fawn colour. A small quantity of the nitrosoamine warmed with phenol and concentrated sulphuric acid gave a deep blue solution, which, on dilution, gave a red, opalescent liquid, turning blue on being rendered alkaline.

Preparation of α-Anilinomyristic Acid.

Thirty grams (1 mol.) of α-bromomyristic acid and 32 grams (3½ mols.) of aniline were heated together in a flask immersed in boiling water for eight hours. The product was worked up as described for the preparation of α-anilinostearic acid (p. 2435), and the acid purified by crystallisation from a mixture of alcohol and ethyl acetate, from which it separated in nodular aggregates melting at 142—143° (compare Hell and Twerdomedoff, *Ber.*, 1889, **22**, 1748). (Found, N = 4·79. Calc., N = 4·39 per cent.)

Tridecylaniline, $C_{13}H_{27}\cdot NH\cdot C_6H_5$.

The α-anilinomyristic acid was heated in quantities of 5 grams in a flask immersed in a metal-bath exactly as described for the preparation of heptadecylaniline and pentadecylaniline (pp. 2435, 2437), the course of the decomposition being similar in all three cases. The product resulting from the action of heat on 16 grams of anilinomyristic acid was distilled under 35 mm. pressure:

240—245°	few drops only.	260—280°	1·5 grams.
248—255°	10·5 grams.	Undistilled residue	1·7 ,,

The fraction 248—255° was redistilled under 35 mm. pressure, when 9·8 grams, boiling at 250—255°, were obtained, which solidified to long, flat needles, melting at 23—24°. This corresponds with a 71 per cent. yield of the theoretical. A portion boiling at 251° was collected separately for analysis:

0·1512 gave 0·4582 CO_2 and 0·1632 H_2O. C = 82·65; H = 11·99.
0·2052 „ 9·6 c.c. N_2 (moist) at 15° and 766 mm. N = 5·52.
$C_{19}H_{33}N$ requires C = 82·91; H = 12·00; N = 5·09 per cent.

Tridecylaniline is readily soluble in alcohol, ether, benzene, chloroform, acetone, or light petroleum, and crystallises from rectified methyl alcohol in long needles, melting at 23—24°. It is insoluble in water or hydrochloric acid, but dissolves readily in concentrated sulphuric acid. It boils at 251°/35 mm.

The *hydrochloride*, $C_{13}H_{27}\cdot NH\cdot C_6H_5,HCl$, was prepared by passing dry hydrogen chloride into a solution of 1·5 grams of the amine in 50 c.c. ether until saturated. Light petroleum was then added to the ethereal solution, and the ether evaporated, when, on allowing the resulting solution to cool, the hydrochloride separated in glistening thin plates. It is readily soluble in alcohol, chloroform, or benzene in the cold, is insoluble in cold acetone or ether, and crystallises from light petroleum (b. p. 60—80°) in glistening, thin plates, melting at 94·5—95·5°. When heated with water, it melts but does not dissolve, and the water becomes strongly acid.

0·3060 Gram, suspended in hot water, required 9·8 c.c. $N/10$-NaOH, using methyl-orange as indicator, whereas this amount of the compound $C_{13}H_{27}\cdot NH\cdot C_6H_5,HCl$ requires 9·8 c.c. $N/10$-NaOH.

The *acetyl* derivative, $C_{13}H_{27}\cdot N(CH_3\cdot CO)\cdot C_6H_5$, was prepared by the interaction of the amine and acetic anhydride, as described for the preparation of the other acetyl derivatives:

0·1852 gave 7·6 c.c. N_2 (moist) at 15° and 756 mm. N = 4·77.
$C_{21}H_{35}ON$ requires N = 4·41 per cent.

Acetotridecylanilide is readily soluble in all the common organic solvents, and crystallises from its solution in dilute methyl alcohol when cooled in a mixture of ice and salt, in flat needles, melting at 31—32°.

The *nitrosoamine*, $C_{13}H_{27}\cdot N(NO)\cdot C_6H_5$, prepared in a manner similar to the other two nitrosoamines, was crystallised from methyl alcohol:

0·1520 gave 12·5 c.c. N_2 (moist) at 19·5° and 769 mm. N = 9·41.
$C_{19}H_{32}ON_2$ requires N = 9·21 per cent.

Phenyltridecylnitrosoamine is readily soluble in chloroform, ether, light petroleum, or benzene in the cold, sparingly so in cold alcohol, and crystallises from methyl alcohol in fawn-coloured, glistening plates, melting at 39—40°. It gives a well-marked Liebermann's reaction, the colour changes being similar to those given by the other two nitrosoamines.

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CCLI.—*The Reduction of Chloric Acid.*

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THE reduction of chlorates or of chloric acid has been the subject of a considerable number of investigations. In general, it has been found that a chlorate, such as potassium chlorate, is readily reduced by zinc and sulphuric acid, but according to Tommasi (*Compt rend.*, 1903, **136**, 1005) the salt is not reduced by sodium amalgam in acid, alkaline, or neutral solutions, whilst, according to Hendrixson (*J. Amer. Chem. Soc.*, 1904, **26**, 747), the same agent has a slight reducing action.

Experiments performed in repetition of this work showed that in presence of excess of a strong acid the chlorate was readily reduced by sodium amalgam, whilst even in alkaline solution reduction could be brought about by the introduction of other metals, such as platinum, copper, iron, etc. In the latter case the effect of addition of one of the metals may be regarded as being due to its influence on the electric potential of the hydrogen evolved. The values of the E.M.F. were determined of a cell containing a solution of potassium chlorate, in which sodium amalgam was used as the anode, and a series of other metals as cathode, and the metals tabulated in the order of the numbers obtained, namely, platinum, copper, iron, nickel, lead, zinc, mercury. It was found that potassium chlorate was reduced when a cathode giving a high value of the E.M.F. was used, whilst reduction did not take place when the latter fell below a certain value.

In alkaline solution therefore reduction appears to depend on the activity of the hydrogen used as measured in terms of electric potential, a result which is in agreement with those of Tafel (*Zeitsch. physikal. Chem.*, 1900, **34**, 187) and others.

In acid solution, however, the conditions are more complex, and other factors than the activity of the hydrogen are involved. By addition of excess of sulphuric acid to a solution of potassium chlorate, reduction is easily effected with sodium amalgam. If, on the other hand, a dilute solution of chloric acid prepared by the action of sulphuric acid on barium chlorate, and free from any other acid, is acted on by sodium amalgam, reduction is not effected, whilst in the presence of other strong acids reduction takes place. Similar results were obtained by employing other reducing agents; methyl alcohol, for example, gave no reduction after being left in contact with a dilute solution of chloric acid for a fortnight, although in the presence of sulphuric acid reduction was readily effected. Similarly, Burchard (*Zeitsch. physikal. Chem.*, 1888, **2**, 823) has shown that mixed dilute solutions ($N/50$ or $N/100$) of chloric and hydriodic acids produce no iodine after keeping for several days. The case is therefore one of some complexity, and it is evident that the presence and concentration of hydrogen ions is an important factor in the reaction. The following experiments were undertaken with a view to the elucidation of this point.

The question of the interaction of chloric acid in a solution containing some oxidisable substance has been the subject of a number of investigations. Burchard (*loc. cit.*) investigated the action of chloric, bromic, and iodic acids on hydriodic acid. He found that the reaction with chloric acid was very much slower than in the case of the other two acids, and that in order that it should proceed with a sufficient velocity it was necessary that the solutions should be so concentrated and the time of action so long that the exact nature of the reaction could not be determined. The presence of other acids in these reactions which did not take part in the reaction was found to have an accelerative effect in proportion to the "strengths" of the acids.

Pendlebury and Seward (*Proc. Roy. Soc.*, 1889, **45**, 396) investigated the reaction between chloric, hydrochloric, and hydriodic acids. They found that dilute solutions of chloric and hydrochloric acids, when mixed together, slowly evolve chlorine and oxides of chlorine, that the rate varies with the quantity of chloric acid in the first place directly, as it is the substance decomposed, and in the second place with a small acceleration proportional to the quantity. Further, variation in the quantity of hydrochloric acid has an effect (1) of a secondary order as above, namely, accelerative, and (2) an effect both primary and secondary on the decomposition of chloric acid by hydrochloric acid.

Schlundt (*Amer. Chem. J.*, 1895, **17**, 754) showed that in the reaction between potassium chlorate, potassium iodide, and hydrochloric acid, the effect of increase of concentration of potassium iodide was about the same as an equivalent increase in concentration of potassium chlorate, but increase of the acid caused a greater increase in velocity. He further investigated the influence of other acids, and found that they exerted an accelerative influence in the order: hydrobromic, hydrochloric, nitric, and sulphuric.

Bray (*J. Physical Chem.*, 1903, **7**, 92) found that the rate at which iodine is liberated from a mixture of potassium chlorate, potassium chloride, potassium iodide, and hydrochloric acid is proportional to the concentration of the chlorate and to the square of the concentration of hydrogen ions, and is a linear function of the concentration of chlorine and of potassium iodide; this corresponds with the equations:

$$ClO_3 + Cl + 2H = ClO_2H + ClOH,$$
$$ClO_3 + I + 2H = ClO_2H + IOH,$$

followed by instantaneous oxidation of the hydriodic acid by their products.

A similar investigation was made by Sand (*Zeitsch. physikal. Chem.*, 1904, **50**, 465), who measured the rate of liberation of chlorine from a mixture of potassium chlorate and hydrochloric acid at 70°, and found the reaction to be quinquemolecular, corresponding with the equation:

$$ClO_3 + 2H + 2Cl = ClO + 2HOCl,$$

the hypochlorous acid then reacting instantaneously with hydrochloric acid to produce chlorine. On the other hand, Luther and McDougal (*Zeitsch. physikal. Chem.*, 1906, **55**, 477) find that the reaction velocity of a mixture of chloric and hydrochloric acids is inversely proportional to the square root of the concentration of chlorine, and consider that the reaction:

$$ClO_3 + 2H + Cl = ClO_2 + \tfrac{1}{2}Cl_2 + H_2O$$

is involved.

It is evident from the above that the decomposition of chloric acid is not of a simple nature, especially in view, also, of the unsatisfactory results obtained when it is attempted to apply the ordinary equations for the order of reactions to this decomposition.

In this it is analogous to the case of bromic acid investigated by Ostwald, Meyerhoffer, and others.

It seemed probable to the author of the present communication that the complexity of these reactions was due to the nature of the accelerative influence of the acid, other than chloric, present in solution. Consideration of some of the preliminary experiments quoted above led to the hypothesis that the reduction of chloric acid might involve the decomposition of the non-ionised molecule of chloric acid as the first stage of the reaction. If this were the case, addition of a second acid should increase the velocity of reduction of chloric acid by suppressing its ionisation, and consequently increasing the concentration of non-ionised chloric acid.

It was shown by Burchard and by Schlundt that the effect of adding acids, such as sulphuric and nitric, was to stimulate the reaction in the order of the strengths of the acids. In view of the considerations just mentioned, such stimulating effect may be due (1) to the mass-action of the second acid in suppressing the ionisation of the chloric acid, or (2) to the purely catalytic influence of the hydrogen ions, the concentration of which is increased by addition of the second acid, or (3) to both. Moreover, when hydrochloric acid is the second acid employed, and the solutions are moderately concentrated, the conditions are still further complicated, since the hydrochloric acid has apparently both a primary influence (that is, it takes part directly in the decomposition of the chloric acid) and a secondary (catalytic) influence.

The following experiments on the velocity of reduction of chloric acid were made with the view of elucidating the nature of the stimulating effect of the second acid. Considerable difficulty was experienced in finding a suitable reaction owing to the extreme slowness of the decomposition, chloric acid being very much more stable than bromic acid at the same concentrations, and for this reason it was found impossible to use the reaction with hydriodic acid, which has been much investigated in the case of bromic acid, and which otherwise would have been comparatively easy to measure.

EXPERIMENTAL.

Preliminary experiments were made on the reduction of chloric acid with methyl alcohol in the presence of silver nitrate and a second acid, and determining the extent of the reaction by weighing the silver chloride formed. Experiments were made in which the strength of the second acid was varied, and it was found that the velocity of reduction increased with increase of the concentration of the second acid added, and that the accelerating influence of the acids was in the order of their strengths.

It was therefore attempted to establish a numerical relation between the acceleration due to the acid added and its affinity-constant, by measuring the velocity of reduction of chloric acid in presence of various accelerating acids.

In the following experiments, two reactions were measured, one in comparatively concentrated solutions (normal) and at comparatively high temperature (35°), and the other at lower concentrations and temperature (decinormal and 25°). In both cases it was found that the measurement of the reaction was a matter of considerable difficulty, and that therefore a high degree of accuracy was impossible, but it was hoped that the results would be such as to indicate a definite relation between the acceleration and "strengths" of the acids.

The first reaction was that of chloric acid and methyl alcohol, and was conducted in the following manner.

A mixture of 20 c.c. of N-chloric acid, 10 c.c. of methyl alcohol, and 70 c.c. of N-acid was placed in a tube which was kept in a thermostat at 35°. From this, 10 c.c. were withdrawn every twenty-four hours, neutralised with chalk, filtered, washed, and the filtrate titrated with $N/100$-silver nitrate solution. Two experiments were made for each acid, and the mean of the two readings was taken.

A blank experiment was then made in which the catalysing acid was replaced by water, and the velocity of the reaction was found to be practically zero. The following table gives the readings for the four acids, nitric, sulphuric, benzenesulphonic, and oxalic (assuming in the latter case that the oxalic and chloric acids do not interact under these conditions), where x = the amount of reaction in terms of 0·1 c.c. $N/100$-silver nitrate, being in each case the mean of two readings, and the time is given in days.

Nitric Acid.

Time.	x.	Acceleration.
1	29·5	—
2	54·5	25·0
3	77·5	24·0
4	100·0	23·5
5	128·0	24·6
6	152·0	24·5
7	—	—
8	201·5	24·5

Mean acceleration (HNO_3 = 100), 100.

Sulphuric Acid.

Time.	x.	Acceleration.
1	17·5	—
2	28·0	10·5
3	38·5	10·5
4	48·0	10·1
5	57·0	9·9
6	68·0	10·1
7	—	—
8	89·0	10·2

Mean acceleration (HNO_3 = 100), 42.

Benzenesulphonic Acid.

Time.	x.	Acceleration.
1	19	—
2	33	14·0
3	43	12·0
4	59	13·3
5	72	13·2
6	—	—
7	94	12·5

Mean acceleration (HNO_3 = 100), 53.

Oxalic Acid.

Time.	x.	Acceleration.
1	6	—
2	8	2·0
3	8	1·0
4	13	2·3
5	13	1·8
6	14	1·6
7	20	2·3
8	21	2·1

Mean acceleration (HNO_3 = 100), 7·8

In the blank experiment, without addition of acid, it was found that after thirteen days the amount of reaction was equivalent to 0·5 c.c. $N/100$-silver nitrate solution, and therefore in calculating the accelerations due to the presence of the above acids at any time it was assumed that the corresponding amount of action in the blank experiment was negligible. The "acceleration" may be regarded therefore as equivalent to the velocity in each case. The values of the acceleration at any particular time were found by subtracting from the amount of reaction which had taken place at the end of that time, the corresponding amount at the end of the first day, and dividing by the time. The amount of reaction taking place during the first day was neglected owing to the unavoidable presence of a trace of chloride at the beginning of the experiment.

The acceleration constants thus obtained are in the order of the strengths of the acids used, although not numerically comparable with the affinity-constants. Close agreement, however, was not to be expected, owing to the conditions of concentration and high temperature used. It was found impossible to obtain satisfactory results with other acids, owing in some cases to the conditions of experiment, and in others to the reaction being too slow to measure.

The second reaction studied was that of chloric acid and ferrous sulphate, which took place in decinormal solution with sufficient rapidity at 25° to be conveniently measured. The experiment tube contained a mixture of 20 c.c. of $N/10$-chloric acid, 20 c.c. of $N/5$-ferrous sulphate solution, and 60 c.c. of $N/10$-acid. After mixing, 10 c.c. were withdrawn and titrated with potassium permanganate, the titration repeated, the experiment tube containing the mixture placed in a thermostat at 25°, and the time noted. After a period of forty-five minutes, 10 c.c. were withdrawn and titrated. The reading was repeated, and the mean value recorded. Some difficulty was experienced in obtaining a good end-point in the permanganate titration owing to the presence of a small quantity of hydrochloric acid produced by the reduction of the chloric acid. It was attempted to use a large excess of manganese sulphate, but extreme difficulty was experienced in judging the colour in presence of the solution of this salt, and it was finally found more accurate to dilute the solution largely with water and to titrate in a porcelain dish, judging the colour by looking through a depth of the liquid.

The solution of chloric acid was prepared as before by the action of sulphuric acid on barium chlorate, the barium sulphate being removed by filtration. The solution was tested for excess of sulphate or barium, and then standardised with N-potassium hydroxide. The ferrous sulphate was prepared by dissolving pure crystals of the salt in water free from air, the solution being kept out of contact with air under a layer of benzene.

A blank experiment was made in which the accelerating acid was replaced by water, and the acceleration due to each acid was found by subtracting the amount of reaction which had taken place in time T in the blank experiment from the corresponding amount in each of the "acid" experiments. The results were tabulated, and the acceleration constants reduced to HCl = 100. The results obtained were as follows, where A = original concentration of ferrous sulphate in terms of 0·1 c.c. N/100-permanganate, and is the mean of two readings, and x_1, x_2 are the readings for the concentration after time T, X being the mean; T = forty-five minutes.

Acid.	A.	x_1.	x_2.	X.	$A-X$.	Acceleration.	Acceleration, HCl = 100.
No acid	426·5	375	376	375·5	51·0	—	—
HCl	422·0	248	247	247·5	174·5	123·5	100
HBr	430·0	245	247	246·0	184·0	133·0	108
HNO_3	422·5	265	266	265·5	157·0	106·0	86
H_2SO_4	425·0	279	286	282·5	142·5	91·5	74
$C_6H_5{\cdot}SO_3H$	426·0	257	256	256·5	169·5	118·5	97
$CCl_3{\cdot}CO_2H$	425·0	265	265	265·0	160·0	109·0	88
$CHCl_2{\cdot}CO_2H$	427·5	328	329	328·5	99·0	48·0	39
$CH_2Cl{\cdot}CO_2H$	426·0	362	360	361·0	65·0	14·0	11

The acceleration constants thus obtained, compared with the corresponding affinity constants found by the hydrolysis of methyl acetate, are as follows:

	Acceleration constant.	Hydrolysis.	
HCl	100	100	
HBr	108	98	or 111 by sugar inversion.
HNO_3	86	92	
H_2SO_4	74	74	
$C_6H_5{\cdot}SO_3H$	97	98	
$CCl_3{\cdot}CO_2H$	88	68	
$CHCl_2{\cdot}CO_2H$	39	23	
$CH_2Cl{\cdot}CO_2H$	11	4·3	

The agreement between the acceleration constant and affinity constant is as close as would be expected, considering the nature of the reaction investigated, except in the case of the chloroacetic acids. It was thought that the high result obtained in each case with these acids might be due to the presence of hydrochloric acid formed by their hydrolytic decomposition, but the solutions were tested after the experiment with silver nitrate solution, and gave no precipitate.

The effect of variation in quantity of the catalysing acid was then examined with the view of ascertaining whether the velocity was affected in any marked degree by the presence of small quantities of the acid.

The experiments were conducted as in the last series.

The experiment tube contained a mixture of 20 c.c. of N/10-chloric acid and 20 c.c. of N/5-ferrous sulphate solution, and a variable quantity of sulphuric acid dissolved in 60 c.c. of water, making a total of 100 c.c.

The following results were obtained:

No. of mols. H_2SO_4 to 1 mol. $HClO_3$.	*A*.	x_1.	x_2.	*X*.	*A* – *X*.	Acceleration.
3	425	279	286	282·5	142·5	91·5
$\frac{1}{2}$	418	343	345	344	74	23·0
$\frac{1}{5}$	417·5	354	356	355	62·5	11·5
$\frac{1}{20}$	417	360	361	360·5	56·5	5·5

Finally, experiments were made on the influence of neutral salts on the velocity of the same reaction. The conditions of experiment were the same as before; the experiment tube in each case contained 20 c.c. of *N*/10-chloric acid, 20 c.c. of *N*/5-ferrous sulphate solution, and 60 c.c. of an *N*/10-solution of the salt.

The following results were obtained:

Salt.	*A*.	x_1.	x_2.	*X*.	*A* – *X*.	Acceleration.
KCl.................	415·0	363	364	363·5	51·5	0·5
KNO_3................	411·0	357	357	357·0	54·0	3·0
Na_2SO_4	413·0	374	375	374·5	38·5	– 12·5
K_2SO_4................	416·5	379	378	378·5	38·0	– 13·0
$KClO_3$................	398·0	263	265	264·0	134·0	83·0
$NaClO_3$	410·0	276	278	277·0	133·0	82·0

It is evident from these results that a neutral salt containing no common ion accelerates the reaction to a very small degree, whilst a salt containing a ClO_3 ion accelerates it very considerably. In order further to examine the reaction with a solution of potassium chlorate, an experiment was made under the same conditions as before, in which no chloric acid was present, the experiment tube containing 20 c.c. of *N*/5-ferrous sulphate solution and 80 c.c. of *N*/10-potassium chlorate solution, but it was found that the amount of reaction after forty-five minutes was practically nil. The influence of potassium and sodium sulphates on the velocity of the reaction is somewhat remarkable. Both salts retard the reaction and approximately to the same degree. This may, perhaps, be due to the formation of less easily oxidisable complex molecules with the ferrous sulphate analogous to ferrous ammonium sulphate.

Summary and Conclusions.

(1) Chloric acid is not reduced by sodium amalgam in dilute solutions, but is reduced in the presence of strong acids.

(2) A dilute solution of chloric acid in the presence of methyl alcohol is not reduced even when the mixture is kept for several days, but in the presence of strong acids reduction takes place.

(3) The rate of reduction of chloric acid by methyl alcohol is extremely slow even in normal solutions, but is accelerated by

addition of strong acids, the order in which these acids accelerate the reaction being that of their relative "strengths."

(4) The reaction between chloric acid and ferrous sulphate in decinormal solution is accelerated by the addition of other acids, the acceleration produced being a function of the "strengths" of the acids.

(5) The same reaction is accelerated in a small degree by neutral salts containing no ion common with any taking part in the reaction. It is accelerated in a large degree by chlorates, and is retarded by sulphates.

It has been suggested above that the accelerative influence of the second acid may be of two kinds, and hence that this influence may be open to two theoretical interpretations. On the one hand, the reaction may be "ionic," the reduction being that of the ClO_3 ion, and the influence of addition of other acids being due to the purely catalytic influence of hydrogen ions. On the other hand, the primary reaction may be the breaking down of the non-ionised chloric acid molecule, which would be accelerated by the addition of other acids in virtue of the mass-action of the hydrogen ions. With regard to the addition of neutral chlorates, it has been shown above that these accelerate the reaction to a considerably greater degree than salts containing no ion common with any of those taking part in the reaction. This accelerative influence is similarly open to both interpretations; it may be due to the mass-action of the ClO_3 ion by which the concentration of the non-ionised chloric acid would be increased, or, since hydrogen ions are present, it may be due to the increase of total concentration of the substance undergoing reduction, namely, the ClO_3 ion. It is evident, however, that free acid is essential to the reaction, since a neutral chlorate does not appear to be affected by the reducing agents employed. Hence, if the reaction is "ionic," it must be assumed that in the absence of catalysing hydrogen ions, the reaction is too slow to measure.

With regard to the experiments given in the present communication, the most important evidence is in the relation of acceleration constants to affinity constants. Chloric acid, according to the conductivity measurements of Ostwald, is a strong acid having an affinity constant of 98, compared with 100 for hydrochloric acid. In view of this, and in view also of the great uncertainty of behaviour of strong acids in presence of their salts (and in general of solutions of mixed strong electrolytes containing a common ion), it is improbable that any close agreement would exist between the acceleration and affinity constants of the acids if the accelerative effect were due to the mass-action of hydrogen ions. Hence the above results seem to favour the view that the reaction is an ionic one, and that the accelerative influence of the second acid is due to the catalytic action of the hydrogen ions.

Several attempts were made to devise an experiment which would exclude one or the other of the above interpretations, such as the use of a non-ionising solvent, an experiment which would have been of great value in deciding the point. Although many solvents were tried, however, none was found which would meet the requirements of the experiment.

In conclusion, I wish to express my sincere thanks to Dr. H. J. H. Fenton for valuable criticism and advice.

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CCLII.—*The Addition of Bromine to Unsaturated Compounds. Part II.*

By JOHN JOSEPH SUDBOROUGH and JOHN THOMAS.

IN continuation of the work already published (this vol., p. 715) we have examined the rate of addition of bromine to the following acids: Cinnamylidene- and *allo*cinnamylidene-acetic acid, sorbic acid, δ-phenyl-Δ^{α}-, -Δ^{β}-, and -Δ^{γ}-pentenoic acids, hydrosorbic acid, crotonic, angelic, tiglic, β-dimethylacrylic, and trimethylacrylic acid.

The method of procedure was exactly the same as that used in the earlier work, and the carbon tetrachloride and bromine were purified in the same manner. A control experiment made with brassidic acid gave values for K varying from 3·0 to 6·9, as compared with the previous values, 3·1 to 7·4. Although the new bromine and carbon tetrachloride gave values for brassidic acid which were very similar to the values obtained previously, it was found that when cinnamic acid was used, the values obtained were considerably lower than the earlier values, namely, $1{\cdot}02\times10^{-5}$ to $2{\cdot}94\times10^{-5}$, as compared with $0{\cdot}9\times10^{-4}$ to $2{\cdot}6\times10^{-4}$. We have not been able to ascertain the reason for this difference, but we have been able to show that the presence of moisture facilitates the addition of bromine. This is best shown in the case of the experiments with crotonic acid:

	K.
Dry carbon tetrachloride	$4{\cdot}68\times10^{-6}$ to $6{\cdot}16\times10^{-6}$
Moist ,, ,, ...	$7{\cdot}31\times10^{-5}$ to $13{\cdot}7\times10^{-5}$

The following table gives a list of the values of K obtained for the different acids at 15°:

Olefine Acids.

Acids and formula.	Series.	Maximum time.	No. of titrations.	$1/t\,.\,x/a(a-x)$.	
				Minimum.	Maximum.
Crotonic, $CHMe:CH\cdot CO_2H$ ……	*a*	189 hours	4	$4\cdot68\times10^{-6}$	$6\cdot16\times10^{-6}$
Angelic, $CHMe:CMe\cdot CO_2H$ ……	*a*	145 ,,	4	$0\cdot83\times10^{-4}$	$1\cdot9\times10^{-4}$
Tiglic, $CHMe:CMe\cdot CO_2H$ ……	*a*	168 ,,	4	$1\cdot3\times10^{-5}$	$9\cdot9\times10^{-5}$
β-Dimethylacrylic,	*a*	6 ,,	3	$5\cdot8\times10^{-3}$	$7\cdot0\times10^{-3}$
$CMe_2:CH\cdot CO_2H$ ……………	*b*	6 ,,	4	$3\cdot1\times10^{-3}$	$7\cdot3\times10^{-3}$
Trimethylacrylic,					
$CMe_2:CMe\cdot CO_2H$ ……………	*a*	8·5 ,,	4	$1\cdot1\times10^{-2}$	$2\cdot2\times10^{-2}$
δ-Phenyl-Δ^{β}-pentenoic,	*a*	0·5 ,,	4	$3\cdot1\times10^{-1}$	$3\cdot7\times10^{-1}$
$CH_2Ph\cdot CH:CH\cdot CH_2\cdot CO_2$ …	*b*	0·5 ,,	3	$6\cdot2\times10^{-2}$	$2\cdot2\times10^{-1}$
δ-Phenyl-Δ^{γ}-pentenoic,	*a*	60 secs.	4	45·7	82·3
$CHPh:CH\cdot CH_2\cdot CH_2\cdot CO_2H$ …	*b*	31 ,,	4	35·5	60·3
Hydrosorbic,	*a*	60 ,,	4	$1\cdot3\times10^{2}$	$3\cdot3\times10^{2}$
$CH_2Me\cdot CH:CH\cdot CH_2\cdot CO_2H$ …	*b*	20 ,,	4	$2\cdot4\times10^{2}$	$3\cdot9\times10^{2}$

Diolefine Acids, with Conjugate Double Bonds.

Acids and formula.	Series.	Maximum time.	No. of titrations.	Minimum.	Maximum.
Sorbic,	*a*	0·66 hours	3	$1\cdot03\times10^{-2}$	$6\cdot8\times10^{-2}$
$CHMe:CH\cdot CH:CH\cdot CO_2H$ …	*b*	0·66 ,,	4	$1\cdot1\times10^{-2}$	$12\cdot2\times10^{-2}$
Cinnamylideneacetic	*a*	1·0 ,,	3	$2\cdot21\times10^{-2}$	$2\cdot63\times10^{-2}$
$CHPh:CH\cdot CH:CH\cdot CO_2H$ …	*b*	4·5 ,,	4	$0\cdot97\times10^{-2}$	$1\cdot3\times10^{-2}$
*allo*Cinnamylideneacetic ………	*a*	1·05 ,,	4	$2\cdot56\times10^{-2}$	$3\cdot1\times10^{-2}$
	b	1·25 ,,	4	$2\cdot9\times10^{-2}$	$3\cdot5\times10^{-2}$

The αβ-unsaturated acid, δ-phenyl-Δ^{α}-pentenoic acid,

$$CH_2Ph\cdot CH_2\cdot CH:CH\cdot CO_2H,$$

combines with bromine very slowly in the dark. Immediately after mixing, the amount of bromine used up corresponded with 0·5 c.c. of the thiosulphate solution, and even after 190 hours the amount of thiosulphate required was the same. The acid thus combines with bromine even less readily than does cinnamic acid. The following values were obtained for the two acids when the addition of bromine was allowed to take place in daylight; the two series of experiments were conducted side by side in order that the results should be strictly comparable:

Cinnamic Acid ($a=26\cdot15$).

t (hours).	$a-x$.	$1/t\,.\,x/a(a-x)$.
0·5	16·7	$4\cdot33\times10^{-2}$
1·0	12·7	4·05
1·5	8·15	5·63
2·0	5·5	7·18

δ-Phenyl-Δ^{α}-pentenoic Acid ($a=26\cdot15$).

t (hours).	$a-x$.	$1/t\,.\,x/a(a-x)$.	t (hours).	$a-x$.	$1/t\,.\,x/a(a-x)$.
0·5	24·8	$4\cdot16\times10^{-3}$	0·5	24·8	$4\cdot16\times10^{-3}$
1·0	23·95	3·51	1·0	23·5	4·31
1·5	22·95	3·56	1·5	22·0	4·81
2·0	22·20	3·40	2·0	20·8	4·92

The results prove that in daylight bromine combines with the δ-phenyl-Δ^{α}-pentenoic acid less readily than it does with cinnamic acid.

The points to which we wish to draw attention in connexion with the results tabulated above are:

(1) The values confirm the generalisation drawn previously (p. 719), namely, that αβ-unsaturated acids combine with bromine far less readily than the isomerides, in which the double linking is further removed from the carboxylic group.

(2) The introduction of methyl substituents, attached to the carbon atoms between which the olefine linking exists, facilitates the addition of bromine to an appreciable extent.

(3) When the acid contains conjugated olefine linkings, one of which is in the αβ-position with respect to the carboxylic group, the addition of bromine takes place more readily than when the αβ-ethylene linking alone is present. In the examples we have examined, namely, sorbic, cinnamylideneacetic, and *allo*-cinnamylideneacetic acids, it is known that the two atoms of bromine are added on in the αδ-positions, and the reaction is thus not strictly comparable with the addition of bromine to cinnamic acid, where the bromine attaches itself at the αβ-position.

Preparation of the Acids.

1. Cinnamylidenemalonic acid was prepared by the method described by Riiber (*Ber.*, 1904, **37**, 2274), with the exception that the mixture of equal weights of malonic acid, quinoline, and cinnamaldehyde were kept in a stoppered bottle for three weeks instead of the two recommended by Riiber. The reduction of the substituted malonic acid was carried out according to Riiber's method, using pure mercury for the preparation of the amalgam, but the evolution of carbon dioxide and the formation of δ-phenyl-Δ^{β}-pentenoic acid, $CH_2Ph\cdot CH{:}CH\cdot CH_2\cdot CO_2H$, was effected by a somewhat different method, as we had no method of obtaining a pressure of 0·15 mm. (*Ber.*, 1905, **38**, 2746). The dibasic acid (25 grams) was heated in a sulphuric acid bath at 110—115° until the evolution of carbon dioxide had ceased, and the product, which was slightly coloured, was distilled under a pressure of 10—12 mm., when the monobasic acid passed over at 176—182°, and solidified on cooling. The transformation of the βγ-acid into a mixture of αβ- and γδ-unsaturated acids was carried out according to Riiber's directions (*loc. cit.*, p. 2747). The β-hydroxyphenylvaleric acid was removed by making use of its insolubility in hot carbon disulphide, and the oily acid removed by pressing the mixture of acid on a plate. The solid mass, consisting mainly of the αβ- and γδ-acids,

was dissolved in hot carbon disulphide, and, on cooling, crude $\alpha\beta$-acid separated. From 150 grams of $\beta\gamma$-acid, 26 grams of crude $\alpha\beta$-acid were thus obtained, and after some six recrystallisations the acid was quite pure. To obtain the $\gamma\delta$-acid, the carbon disulphide mother liquor was evaporated to dryness, and the acid transformed into the sparingly soluble calcium salt under the conditions described by Riiber. The acid obtained from the calcium salt still contained $\alpha\beta$-acid, and this was removed by crystallisation from carbon disulphide and mechanically removing the characteristic plates of the $\gamma\delta$-acid and crystallising from light petroleum, when 11·5 grams of pure acid, melting at 91°, were obtained.

2. Hydrosorbic acid was prepared as follows. Twenty-five grams of sorbic acid were dissolved in sodium hydroxide solution, and the whole made up to 300 c.c. with water. The solution was transferred to a separating funnel, and placed in a bath at 30—35°. Rather more than the theoretical amount of 3 per cent. sodium amalgam was added in small amounts at a time, and the funnel was shaken vigorously after each addition. The reduction proceeded vigorously at the beginning, but slackened toward the end. The mercury was removed, the solution acidified with hydrochloric acid (1 : 1), and extracted with ether. After removal of the ether, 13 grams of hydrosorbic acid, boiling at 103°/9—10 mm., were obtained. When the distillation was continued, the temperature rose rapidly, but did not become constant.

3. Cinnamylideneacetic and *allo*cinnamylideneacetic acids were prepare by Liebermann's method (*Ber.*, 1895, **28**, 1441). The *allo*-acid was slightly impure, and melted at 115—117°.

4. The β-dimethyl- and trimethyl-acrylic acids were prepared by the methods described previously (Trans., 1909, **95**, 977).

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CCLIII.—*The Viscosity and Density of Caesium Nitrate Solutions.*

By Thomas Ralph Merton, B.Sc. (Oxon).

In recent years the viscosity of salt solutions has been the subject of numerous investigations, which have mainly been directed toward elucidating the relation between viscosity and electrical conductivity. Most of the alkaline nitrate solutions have been investigated (Grüneisen, *Wiss. Abh. Phys. Tech. Reichsanstalt*, 1904, **4**, 239; Applebey, this vol., p. 2000, and others). Very little, however, is known of the viscosity of cæsium salt solutions, with the exception of a single investigation on the viscosity of the chloride solution by Wagner (*Zeitsch. physikal. Chem.*, 1890, **5**, 31).

In the present investigation, the viscosities and densities of cæsium nitrate solutions of different concentrations have been determined at 0°, 10°, 18°, and 25°.

Experimental.

The method used for determining viscosity was that of Poiseuille, that is to say, a determination of the times of flow of the solution through a capillary tube. The precautions which must be observed in order to secure an accuracy of one part in a thousand by this method have been thoroughly investigated by Grüneisen (*loc. cit.*, p. 153) and Applebey (*loc. cit.*), whose method I have followed in this investigation, and to whom I am indebted for much valuable assistance in the progress of the work. Two viscometers of the Ostwald type were used.

For viscometers of this type we have:

$$\frac{\eta \text{ solution}}{\eta \text{ water}} = \frac{(\Delta \text{ solution} - d) \times t \text{ solution}}{(\Delta \text{ water} - d) \times t \text{ water}},$$

where η is the viscosity, Δ the density, t the time of flow of the liquid through the capillary, and d the density of air.

Grüneisen (*loc. cit.*) has shown that, for viscometers of the type used, it is unnecessary to apply any correction for the kinetic energy of the liquid in the capillary.

The determination of time offered no difficulty, and was measured by means of a stop-watch reading to one-fifth second, which kept excellent time throughout the investigation.

In order to prove that the flow of the liquids to be investigated in the viscometers obeyed Poiseuille's law, one of the tubes was calibrated by Grüneisen's method, with the experimental arrangements used by Applebey (*loc. cit.*). The times of flow of equal volumes of water through the capillary under different hydrostatic pressures are given in the following table:

Excess pressure (in mm. of water at 18°).	Total pressure.	Time (in 1/5th secs.).	Pressure × time.
1·0	115·4	4573	5276
7·3	121·7	4338	5280
22·4	136·8	3865	5288
33·5	147·9	3566	5273
45·0	159·4	3298	5258
55·7	170·1	3091	5260
77·0	191·4	2755	5273
83·8	198·2	2663	5278
88·7	203·1	2585	5250
110·1	224·5	2340	5255
134·5	248·9	2115	5265
149·9	264·3	1990	5261

As will be seen, the value pressure × time is constant within the limits of experimental error, showing that the flow of liquid through the tube obeys Poiseuille's law, and that the tube can therefore be used for comparative measurements between the limits of time examined.

The second viscometer used in this work was standardised by careful comparison with the first. For this purpose a nearly saturated solution of cæsium nitrate has unique advantages, as its high density and low viscosity cause it to flow through the tube more rapidly than water. The ratios of the times of flow of the solution and water in the two tubes were compared, with the following results:

	Time of flow, water.	Time of flow, solution.	Time of flow of solution. / Time of flow of water.
Standard tube	4802	4020	0·8371
Tube 7	4132	3459	0·8371

The constancy of the ratio shows that the second tube obeys Poiseuille's law in exactly the same way as the first.

The viscometers were usually cleaned after use by drawing them through a considerable quantity of the purest available water. If, however, the "water constant" or time of flow of water had changed it was usually re-determined for one of the viscometers after each solution), or if any dust had lodged in the capillary, it was cleaned with a mixture of nitric acid and a drop of alcohol, followed by water. The viscometers were dried by drawing dust-free air through them in a hot-air bath.

In this connexion it may be mentioned that the purity of the air in the room in which the viscometers are dried is of considerable importance. On one occasion there was a certain amount of amyl acetate vapour in the room in which the viscometers were dried, owing to some celluloid varnish containing amyl acetate which had been used there. In consequence of this, anomalous results were obtained, and it was not until the drying apparatus was removed to another room that the viscometers again gave their original water value.

Materials Used.—The cæsium nitrate used in this investigation was very kindly lent by the Earl of Berkeley. It was examined spectroscopically, and no trace of any impurity could be found. The water used was the best dust-free water obtainable (the electrical conductivity varied from 1×10^{-6} to 2×10^{-6} mhos.). In making up a solution, the approximate quantity of salt required was placed in a quartz crucible, and heated for about four hours in a quinoline bath at 170°. It was then weighed and dissolved in a known weight of water. The solutions were filtered to remove dust particles.

Determination of Density.—For the determination of density, a pyknometer containing about 12 c.c. of the solution was used. Two settings and two fillings were taken, the pyknometer being weighed against a counterpoise. The pyknometers were "set" in the constant temperature baths in which the viscosity measurements were made. For the densities at 0°, two pyknometers were used, with a small bulb above the capillary to allow for the expansion of the liquid on removing it from the ice, and a glass cap to prevent evaporation. They were set in a jacketed vessel containing crushed ice.

Constant Temperature Baths.—The experiments at 10°, 18°, and 25° were performed in large glass-fronted baths containing about 25 litres of water, vigorous stirring being obtained by means of glass stirrers driven by an electric motor. The temperatures of the baths were verified by means of a standard Goetze thermometer. The 25° bath was heated by a small gas flame, which was governed by a large spiral toluene regulator (Lowry, Trans., 1905, **87**, 1032). The 18° bath was heated by a 16 c.p. electric filament lamp placed in a bath close to the stirrer, and governed by a spiral electric regulator.

The 10° bath was identical with that at 18°, except that it contained in addition a coil of metal tubing, through which water was run, to act as a cooling apparatus. No variation in the temperature of these baths could be detected on the thermometer divided in 1/50°. The 10° bath, with which some trouble was anticipated, was particularly carefully examined with a Beckmann thermometer, but no variation as great as 1/500° could be detected.

The experiments at 0° were performed in a large Dewar vacuum vessel, containing crushed ice and water vigorously stirred. At this temperature rapid stirring was found to be essential in order to prevent accumulation of warmer water at the bottom of the vessel. In the event of a small variation of temperature occurring, a calculated correction can be applied. This correction was found to be about two-fifths second for 1/100°. It is probable that owing to the difficulty of maintaining constant temperature, the results at 0° are not so accurate as at other temperatures.

Density Results.—The results of the density determinations are given in the following tables. As will be seen, the weighings usually agree to within 0·0001, or at most 0·0002, milligram, and therefore the errors in the densities do not exceed 0·00002. Values of $(\Delta - 1)$ – Concentration × Constant are given, from which a sensitive curve can be drawn.

Densities at 0°.

Parts of cæsium nitrate in 100 grams of water.	Mass of solution in pyknometer. 1.	Mass of solution in pyknometer. 2.	Mean sp. gr.	Δ°_{4}.	$(\Delta - 1) - P \times$ 0·0074.
0	12·4743	14·0425	1	0·99987	−0·00013
1·0075		14·1507 14·1507 14·1507	1·00770	1·00757	+0·00010
1·9784		14·2537 14·2537	1·01504	1·01491	+0·00027
4·0208	13·8832	14·4690	1·03037	1·03023	+0·00048
6·2489	14·1033	14·6981	1·04668	1·04654	+0·00030
8·3724	14·3110	14·9144	1·06209	1·06195	+0·00000

Densities at 10°.

Parts of cæsium nitrate in 100 grams of water.	Mass of solution in pyknometer.	Mean sp. gr.	Δ abs.	$(\Delta - 1) - P \times$ 0·0071357.
0	12·5778	1	0·99973	−0·00027
1·0467	12·6761 12·6762 12·6762	1·00782	1·00755	+0·00008
2·1849	12·7823 12·7824 12·7824	1·01626	1·01598	+0·00039
3·2361	12·8800 12·8801 12·8801	1·02403	1·02375	+0·00066
5·7336	13·1084 13·1085	1·04219	1·04191	+0·00100
8·8891	13·3921 13·3920 13·3923	1·06474	1·06445	+0·00102
12·0698	13·6741 13·6742 13·6741	1·08716	1·08687	+0·00075
14·3040	14·7037 14·7037 14·7037	1·10237	1·10207	±0

Densities at 18°.

Parts of cæsium nitrate in 100 grams of water.	Mass of solution in pyknometer.		Mean sp. gr.	Δ abs.	$(\Delta - 1) - P \times$ 0·0070074.
	3.	*N.*			
0	12·5674	8·8160	1	0·99862	−0·00138
1·0060	12·6610 12·6611 12·6610		1·00745		−0·00099
2·1415	12·7656 12·7656 12·7656		1·01577	1·01437	−0·00063
3·1299	12·8562 12·8562		1·02298	1·02157	−0·00036
5·0677	13·0321 13·0322 13·0322		1·03698	1·03555	+0·00004
6·5882		9·2372 9·2371 9·2372	1·04778	1·04633	+0·00017
9·6569		9·4290 9·4290 9·4290	1·06953	1·06805	+0·00038
12·3740	13·6759 13·6758 13·6759 13·6761		1·08820	1·08671	±0·00000
16·6355		9·8456 9·8456 9·8456	1·11679	1·11525	−0·00132

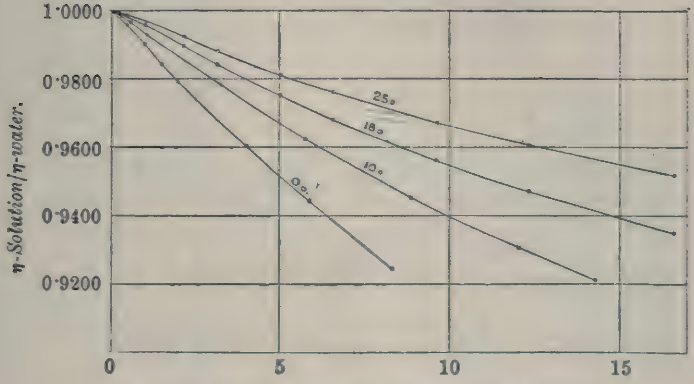
Densities at 25°.

Parts of cæsium nitrate. in 100 grams of water.	Mass of solution in pyknometer.		Mean sp. gr.	Δ abs.	$(\Delta - 1) - P \times$ 0·0068215.
	3.	*N.*			
0	12·5502	8·8043	1	0·99707	−0·00293
1·0060	12·6431 12·6431 12·6430		1·00739	1·00443	−0·00243
2·1415	12·7467 12·7465 12·7466		1·01566	1·01268	−0·00193
3·1299	12·8365 12·8365 12·8365		1·02281	1·01981	−0·00154
5·0677	13·0112 13·0111 13·0112		1·03673	1·03369	−0·00088
6·5882		9·2219 9·2218 9·2219	1·04743	1·04436	−0·00058
9·6569		9·4111 9·4113 9·4114	1·06894	1·06580	−0·00007
12·3740	13·6497 13·6496 13·6497		1·08760	1·08441	−0·00000
16·6355		9·8279 9·8276 9·8279	1·11625	1·11298	−0·00050

Viscosity Results.—The results of the viscosity determinations are given in the following tables. The results are probably correct to ±2 in 5000 at 18°, 25°, and 10°. At 0° the errors are somewhat greater, but the values given are probably correct to ±3 in 5000. In Fig. 1 the relative viscosities are plotted against the concentration. Values of $(1-\eta)-\text{concentration}\times K$ are given, from which a sensitive curve may be drawn. The viscosity in absolute units has also been calculated, the absolute values of water being taken from Thorpe and Rodger's values (*Phil. Trans.*, 1894, *A*, **185**, 397).

At 0° = 0·01778
At 10° = 0·013025
At 18° = 0·010510
At 25° = 0·00891

FIG. 1.



Grams of caesium nitrate in 100 *grams of water.*

Discussion of Results.

It will be seen that at all temperatures the viscosity of cæsium nitrate solutions is less than that of water. It conforms with the rule found for other salts, in that the decrease of viscosity for unit quantity of salt decreases with increase of concentration. The discovery of Grüneisen (*loc. cit.*), that the viscosity curves of all ionised solutions exhibit a change of curvature at the dilute end, has been confirmed in the case of cæsium nitrate. This can be seen in curves in which viscosity is plotted against concentration, but it can be better appreciated by plotting $(1-\eta)/N$ (where N is the normality) against $\sqrt[3]{N}$. In Fig. 2, $1-\eta/N$ is plotted against $\sqrt[3]{\text{normality}}$ at 18°. It is more convenient to plot $\sqrt[3]{N}$ than N, as in this way the dilute end is more extended. It will be seen that the errors in the determination of $(1-\eta)/N$ increase very rapidly towards the dilute end. For example, in a solution

Viscosities at 0°.

Parts of cæsium nitrate in 100 parts of water.	Normality (weight) gram-equivalents in 1000 grams of solution.	$\sqrt{N}$.	Δ rel.	$\frac{\text{Time of flow of solution}}{\text{Time of flow of water}}$ by viscometer No. 5	5	7	7	Mean η (relative).	$1-\eta/N$.	η abs.	$(1-\eta)-P\times$ 0·0093.
0·4920	0·02513	0·2929	1·00376	0·9923	0·9923	—	—	0·9960	0·01591	0·017709	−0·0004
1·0075	0·05120	0·3713	1·00770	0·9826	0·9826	0·9826	—	0·9901	0·01933	0·017603	+0·0008
1·5048	0·07609	0·4238	1·01144	—	—	0·9729	0·9730	0·9841	0·02089	0·017497	+0·0024
1·9784	0·09958	0·4634	1·01504	0·9648	0·9648	0·9651	—	0·9793	0·02073	0·017411	+0·0028
4·0208	0·1984	0·5833	1·03037	0·9320	0·9320	0·9318	0·9318	0·9602	0·02005	0·017063	+0·0038
5·9065	0·2863	0·6590	1·04403	—	0·9042	0·9042	0·0944	0·9441	0·01952	0·016786	+0·0026
8·3724	0·3965	0·7347	1·06209	0·8703	0·9703	0·8703	—	0·9244	0·01908	0·016436	+0·0000

Viscosity at 10°.

											$(1-\eta)-P\times$ 0·005523
0·5723	0·0292	0·3080	1·00427	0·9928	0·9928	0·9928	—	0·9970	0·1027	0·012986	−0·0001
1·0467	0·0532	0·3761	1·00782	0·9857	0·9857	0·9854	—	0·9932	0·1278	0·012936	−0·0010
3·2361	0·1609	0·5439	1·02403	—	—	0·9557	0·9555	0·9786	0·1323	0·012746	+0·0035
5·7336	0·2783	0·6259	1·04219	0·9234	0·9234	0·8236	—	0·9625	0·1347	0·012536	+0·0059
8·8891	0·4190	0·7498	1·06474	0·8880	—	0·8879	0·8879	0·9454	0·1303	0·012314	+0·0055
12·0698	0·5527	0·8206	1·08716	0·8563	0·8563	0·8561	—	0·9309	0·1250	0·012125	+0·0025
14·3040	0·6423	0·8624	1·10237	0·8355	—	0·8355	—	0·9211	0·1228	0·011997	−0·0001

Viscosities at 18°.

Parts of cæsium nitrate in 100 parts of water.	Normality (weight) gram-equivalents in 1000 grams of solution.	$\sqrt[3]{N}$.	Δ rel.	Time of flow of solution / Time of flow of water by viscometer No. 5	5	7	7	Mean η (relative).	$1-\eta/N$.	η abs.	$(1-\eta)-P\times$ 0·004283.
0·4529	0·02314	0·2850	1·00333	0·9952	—	0·9954	0·9954	0·9986	0·06050	0·010495	−0·0005
1·0060	0·0511	0·3711	1·00745	0·9885	—	0·9886	0·9886	0·9960	0·07827	0·010468	−0·0003
2·1415	0·1076	0·4757	1·01577	0·9746	—	0·9746	—	0·9899	0·09386	0·010404	+0·0009
3·1299	0·1557	0·5380	1·02298	0·9623	0·9623	0·9622	—	0·9844	0·10019	0·010346	+0·0022
5·0677	0·2475	0·6278	1·03698	0·9403	0·9403	0·9404	—	0·9752	0·10020	0·010249	+0·0031
6·5882	0·3173	0·6820	1·04778	0·9238	0·9238	0·9242	—	0·9681	0·10053	0·010175	+0·0037
9·6569	0·4520	0·7674	1·06953	0·8940	0·8940	0·8938	—	0·9561	0·09712	0·010049	+0·0025
12·3740	0·5652	0·8269	1·08821	0·8702	0·8702	0·8700	—	0·9470	0·09377	0·009953	0·0
16·6355	0·7321	0·9016	1·11679	0·8371	0·8371	0·8371	—	0·9347	0·08892	0·009336	−0·0071

Viscosity at 25°.

											$(1-\eta)-P\times$ 0·0032.
0·4529	0·02314	0·2850	1·00331	0·9956	0·9956	0·9954	—	0·9988	0·5185	0·008899	−0·0002
1·0060	0·0511	0·3711	1·00739	0·9896	—	0·9897	—	0·9970	0·5871	0·008883	−0·0002
2·1415	0·1076	0·4757	1·01566	0·9775	—	0·9773	0·9773	0·9926	0·6877	0·008844	+0·0006
3·1299	0·1557	0·5380	1·02281	0·9662	—	0·9662	0·9662	0·9882	0·7578	0·008804	+0·0018
5·0677	0·2475	0·6378	1·03673	0·9462	0·9462	0·9464	—	0·9811	0·7636	0·008742	+0·0027
6·5882	0·3173	0·6820	1·04743	—	0·9324	0·9319	0·9319	0·9761	0·7532	0·008697	+0·0028
9·6569	0·4520	0·7674	1·06894	0·9048	0·9048	0·9048	—	0·9671	0·7278	0·008617	+0·0020
12·374	0·5652	0·8269	1·08760	0·8830	0·8830	—	—	0·9604	0·7006	0·008557	0·00
16·6355	0·7321	0·9016	1·11625	0·8529	0·8529	0·8522	—	0·9518	0·6583	0·008480	−0·0050

with a relative viscosity of 0·9980, $(1-\eta)$ would be 0·0020, so that an error of 0·01 per cent. would produce an error of about 4 per cent. in the value of $1-\eta/N$, whereas if the viscosity were 0·9200, a similar error would alter $1-\eta/N$ by less than 0·125 per cent.

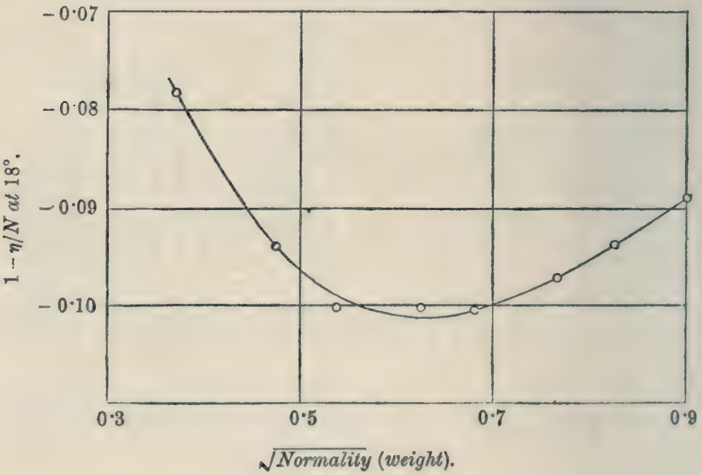
It would be of great interest to discover, if possible, the value of $1-\eta/N$ for infinite dilution, but, as has been shown, the errors increase so rapidly towards the dilute end that it becomes impossible to form any estimate.

Grüneisen (*loc. cit.*) has proposed the formula:

$$\eta-1/N=Ai+B(1-i)+CN,$$

where i is the ratio L/L_0, L and L_0 being the molecular electrical conductivities at concentrations N and 0, and A, B, and C are constants depending on the nature of the salt. Grüneisen has obtained fairly good agreement in his results between the found values of η and those calculated by this formula. I have not been able to find any determinations of the electrical conductivity of cæsium nitrate solutions, and have therefore been unable to make any attempt to apply the formula to my results.

FIG. 2.



From the absolute values calculated from Thorpe and Rodger's (*loc. cit.*) values for water, it will be seen that the change of viscosity produced by a rise in temperature decreases with increasing concentration. Thus, 7 parts of cæsium nitrate in 100 parts of water lower the viscosity about 7·5 per cent. at 0°, but less than 3 per cent. at 25°.

The general form of the viscosity curve is precisely what we should expect from the position of cæsium in the periodic system, a comparison with the viscosities of lithium, sodium, and potassium nitrates, taken from Grüneisen's paper, showing that, qualitatively, the viscosity changes follow the classification of the elements in the periodic system. If we may assume that the viscosity of a solution depends on the mean size of the molecules and ions, we should infer that of the alkali metals the cæsium ion is the smallest, in aqueous solution, that is to say, it has a smaller number of water molecules attached to it than the ions of the other alkali metals. In agreement with this, the cæsium ion is known to possess the largest ionic mobility.

Summary.

The viscosities of cæsium nitrate solutions have been investigated at 0°, 10°, 18°, and 25°. The results confirm in every respect the general principles discovered for other salt solutions.

The densities of the solutions at these temperatures have been determined. In these determinations, no abnormal results have been found. The change of density per unit quantity of salt decreases slightly with an increase of concentration.

The effect of temperature on the viscosity has been examined, and found to decrease with increasing concentration.

With respect to the viscosity of the nitrate solutions, cæsium occupies a position among the alkalis in accordance with its position in the periodic system.

In conclusion, I should like to express my thanks to Mr. H. B. Hartley and Mr. D. H. Nagel for the kind assistance and advice they have given me in this investigation.

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Oxford.

CCLIV.—*The Homogeneous Decomposition of Ozone in the Presence of Oxygen and Other Gases.*

By David Leonard Chapman and Herbert Edwin Jones.

It has been shown by H. E. Clarke and one of us (Trans., 1908, **93**, 1638) that the rate of decomposition of ozone on the surface of glass is so slow that even in moderately small globes the amount of ozone destroyed on the internal surface of the vessel may be neglected in comparison with that decomposed in the interior of the gas. In other words, it has been demonstrated that the conversion of ozone into oxygen under suitable conditions may be assumed to be a homogeneous change without any appreciable error being made. It is the only slow chemical change in the gaseous state which has, as yet, been shown to satisfy the condition of homogeneity under realisable conditions.

Since the quantitative investigation of a chemical change entirely confined to matter in its least complex state might be expected to furnish results of exceptional theoretical significance, an attempt was made by Mr. H. E. Clarke and one of us to construct an apparatus with which the velocity of decomposition of ozone in the presence of oxygen and other gases might be measured; but before the apparatus had been sufficiently perfected to furnish satisfactory results, Mr. Clarke was unfortunately compelled to relinquish the work. The investigation has been continued by the authors of this communication with the aid of a slightly modified and improved form of the apparatus originally designed by Clarke and one of us. Before giving a detailed account of this apparatus, and the mode of conducting an experiment, it will be convenient to state the general conclusions that have been drawn from the results, and to indicate what we believe to be the theoretical significance of these conclusions.

The results demonstrate that:

(*a*) Oxygen, nitrogen, carbon dioxide, and possibly water vapour have no effect on the rate of decomposition of ozone, that is, the rate of decomposition of ozone in the presence of these gases is a function of the concentration of the ozone only.

(*b*) Nitrogen peroxide (Andrews) and chlorine accelerate in a marked degree the decomposition of the gas.

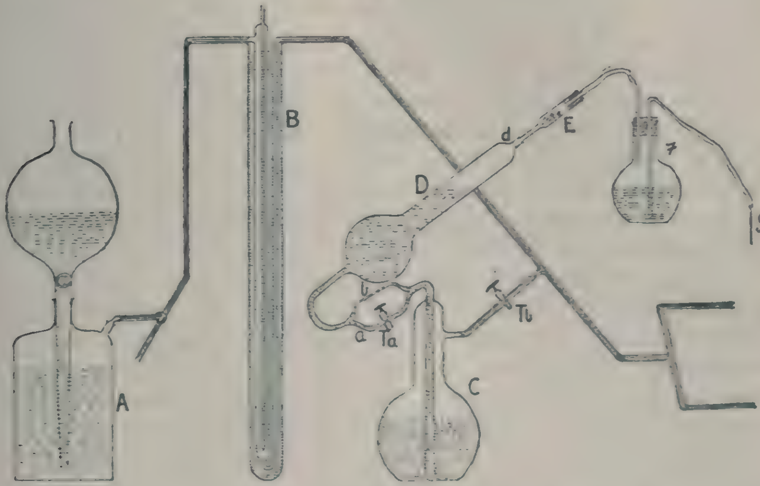
(*c*) If the order of the change can be represented exactly by an integral ordinal number, that number is the second.

In respect of their influence on the rate of decomposition of ozone, gases may therefore be separated into two classes—those which are without effect, and those which act as powerful catalysts. That a classification based on such a striking distinction should be possible lends strong support to the view that the catalytic action of the second class is chemical rather than physical in its nature, since a physical property is generally shared, in a greater or less degree, by all gases. Moreover, nitrogen peroxide and chlorine are substances of which the first is known to react with ozone, and the second is closely related to an element, namely, iodine, which has been shown to be oxidised by ozone.

The facts, so far as they have been made out, indicate that the mechanism of the decomposition of ozone in the absence of catalysts is a simple process, consisting of the conversion of two molecules of ozone during a favourable collision into three molecules of oxygen. Such a view is in harmony with the fact that gases having no chemical action on ozone are without influence on its rate of decomposition (for the number of collisions between pairs of molecules of ozone is almost independent of the diluting gas), and also with the fact that the reaction is of the second order.

A result of exceptional interest is that which relates to the influence of moisture. The discussion of this will be relegated to the experimental section of the paper.

FIG. 1.



EXPERIMENTAL.

The apparatus used for the preparation and collection of the ozonised oxygen is depicted in Fig. 1. The oxygen was prepared by heating potassium permanganate. Dust and carbon dioxide were removed from it by its being passed through a tube packed with glass wool and soda-lime. It was stored in a small gas-holder *A*, which contained concentrated sulphuric acid. The gas-holder was connected by narrow capillary tubing with a Brodie ozone generator *B*, made of thin glass, as recommended by Shenstone (Trans., 1893, **63**, 938). The generator was immersed in dilute sulphuric acid, and its inner tube contained metallic mercury. It was connected by capillary tubing with a vessel *C*, containing concentrated sulphuric acid saturated with ozone. As the ozonised oxygen passed into this vessel, the displaced acid entered the reservoir *D*. The receptacles *D* and *C* were connected by a wide tube *a*, in which a tap T_a was inserted, and also by a tube *b* of very fine bore.

When T_a was closed, the acid entered *D* very slowly, owing to the resistance offered to its motion by the capillary tube, and the rate at which the ozonised oxygen entered the receiver was correspondingly slow. The upper end of *D* was connected with a device by means of which the current of gas could be further regulated. The wide tube *E*, containing powdered potassium hydroxide, was ground into the mouth *d* of the receptacle *D*. *E* was in turn joined by rubber tubing to a flask *F*, containing water, which could be siphoned out drop by drop through the fine capillary tube *G*. By raising and lowering *G*, the rate at which the water siphoned over could be regulated, and the flow of gas through the ozone generator thereby controlled. The potassium hydroxide in *E* served to destroy traces of ozone which would otherwise have attacked the rubber tube. Before use, the apparatus was cleansed with a hot mixture of potassium chromate and concentrated sulphuric acid, and then with hot distilled water, and thoroughly dried.

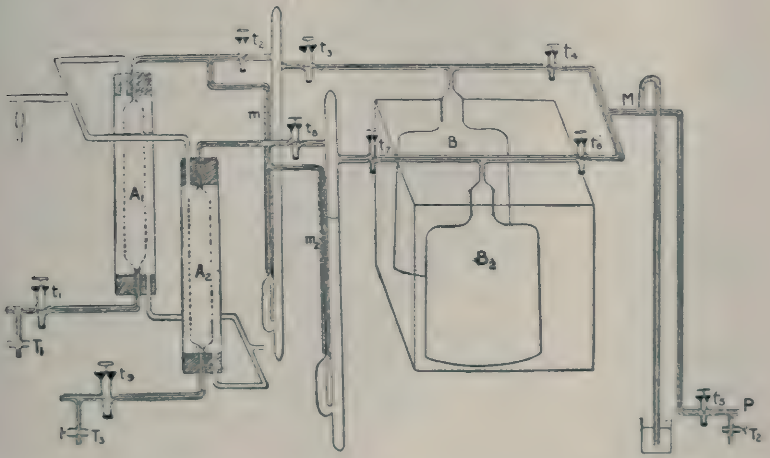
All air was displaced from the apparatus before starting an experiment by a current of oxygen. Oxygen was collected in the gas-holder, and a volume of ozonised oxygen sufficient for one experiment was prepared from it. The tap T_b was then closed, and the oxygen remaining in the gas-holder *A* was allowed to escape. The gas in the receiver *C* was next transferred to the holder *A*, the taps T_a and T_b being left open. It was then again drawn slowly through the ozone generator into the receiver *C*, the coil being in action. The percentage of ozone was appreciably increased by the gas being submitted for a second time to the action of the silent discharge.

The section of the apparatus used to measure the rate of decomposition of the ozone (at 100°) is shown in Fig. 2.

The glass tubes, A_1 and A_2, of about 100 c.c. capacity, in which the ozone was heated, communicated by capillary tubes, on the one side with the previously described section of the apparatus, and on the other with the left-hand limbs of the manometers m_1 and m_2, which contained concentrated sulphuric acid. The right-hand limbs of the manometers were connected by capillary tubes and ground glass joints with two bottles, B_1 and B_2, of about 2 litres capacity each. The corresponding parts of the apparatus were made as nearly alike as possible. The apparatus was connected with an injector pump at *P*, and was provided with a mercury manometer at *M*, as shown in the diagram. Taps T_1, T_2, and T_3, and taps t_1, t_2, t_3, t_4, t_5, t_6, t_7, t_8, and t_9, provided with mercury seals, were inserted in the positions indicated in the figure. The pressure on the right-hand side of the manometers was kept constant by the bottles being immersed in a bath of water at a fixed temperature. The water in the bath was stirred by a current of air, and the temperature was controlled by a delicate electric thermoregulator.

During an experiment the tubes A_1 and A_2 were kept at 100° by means of a current of steam, which entered the jackets surrounding them from above. In a preliminary experiment, it was shown that the temperature of both of the tubes could be raised to that of the steam in the same time. Before the experiments were started, ozonised oxygen was passed through the heated tubes for several hours.

FIG. 2.



Influence of Oxygen on the Rate of Decomposition of Ozone.

The object of the first series of experiments was to ascertain the effect, if any, of varying concentrations of oxygen on the rate of decomposition of the ozone. The method of conducting an experiment was as follows.

A quantity of ozonised oxygen sufficient for one experiment was collected in C, the ozone remaining in the generator and capillary tubes being subsequently driven out through the taps T_1 and T_3 by a stream of oxygen from the holder A.

With the taps t_1, t_9, and T_2 closed, and t_2, t_3, t_4, t_5, t_6, t_7, and t_8 open, the apparatus was exhausted as completely as possible by the injector pump. The taps t_5, t_3, and t_7 were then closed, and oxygen admitted from the holder A through t_1 and t_9 until the volume between the taps t_1 and t_3 and between the taps t_9 and t_7 had been filled. The pump was again set in action, and the taps t_5, t_3, and t_7 cautiously opened. When the limit of exhaustion attainable with the injector pump had been reached, the process described above was repeated, the removal of traces of air from the tubes A_1 and A_2 being thereby ensured.

After the final exhaustion the taps t_5, t_2, and t_8 were closed. By cautiously opening t_1 and t_9, ozonised oxygen was admitted to the tubes A_1 and A_2 from the receiver C, the pressure on both sides of the manometer being maintained the same by the simultaneous admission of air into the bottles B_1 and B_2 through the taps t_5 and T_2. When the manometer M indicated a pressure of a little less than half an atmosphere, t_4 was closed. The ozone left in the capillary tubes on the left-hand side of the taps t_1 and t_9 was displaced by oxygen, and oxygen was then introduced into the tube A_2 by carefully opening the tap t_9, air being at the same time admitted through t_5. The taps t_6 and t_9 were closed when the manometer m indicated a pressure slightly less than an atmosphere.

The tube A_1 was thus filled with ozonised oxygen at the pressure of half an atmosphere, whilst A_2 contained the same amount of ozone, but approximately twice as much oxygen.

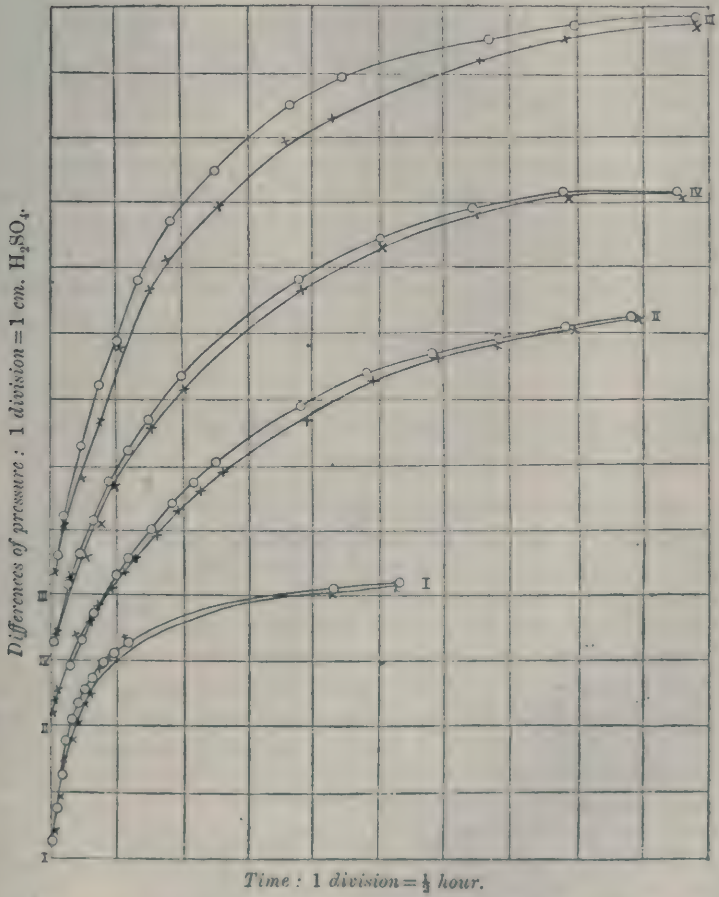
The tubes having been filled, the taps t_2 and t_8 were opened, and a rapid current of steam was passed through the steam jackets. After one and a-half minutes (when the contents of the tubes had attained the temperature of the steam), the taps t_2 and t_8 were closed. The differences of pressure registered by the manometers were noted at regular intervals. Curves were plotted, showing the relation between the increase of pressure in the tubes A_1 and A_2 and the time. It sometimes happened that the total amounts of ozone contained in A_1 and A_2 respectively (as indicated by the total change of pressure) were not exactly equal. In such cases a simple correction was applied in order that the results might be strictly comparable.

The changes of pressure in cm. of sulphuric acid are plotted against the times, and the four pairs of curves thus obtained are shown in Fig. 3. The circles correspond to the changes of pressure in the tube which contained ozonised oxygen at a pressure of half an atmosphere, and the crosses to changes of pressure in the other tube which contained the same amount of ozone per unit volume, but twice as much oxygen. The numbers attached to the curves indicate the order in which the experiments were performed.

These results point decisively to the conclusion that variation in the pressure of the oxygen mixed with ozone is unattended by appreciable alteration in the velocity of decomposition of the latter gas at 100°. This conclusion does not appear to agree with the observations of previous investigators.

S. Jahn (*Zeitsch. anorg. Chem.*, 1906, **48**, 260) and Perman and Greaves (*Proc. Roy. Soc.*, 1908, *A*, **80**, 353) assert that the rate of decomposition of ozone varies approximately inversely as the oxygen-pressure. If the reaction were reversible, this result might be expected; but Perman and Greaves and others have conclusively demonstrated that at 100° it may be regarded as irreversible.*

FIG. 3.



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* Fischer and Braehmer (*Ber.*, 1906, **39**, 940), have recently shown that ozone is formed in small quantities from oxygen at temperatures above 1300°.

In order to explain his results, Jahn has suggested that the decomposition of ozone occurs in two stages, expressible by the equations:

$$O_3 = O_2 + O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$
$$O_3 + O = 2O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

the first stage being rapid and reversible, whilst the second is slow. These assumptions would require that the rate of decomposition of the ozone should be directly proportional to the square of the concentration of the ozone, and inversely proportional to the concentration of the oxygen. Jahn's experiments were carried out at 127°, at which temperature the reaction is bimolecular, according to Warburg (*Sitzungsber. K. Akad. Wiss. Berlin*, 1901, **48**, 1126).

Perman and Greaves, on the other hand, consider that Jahn's hypothesis is not justifiable, and that the alleged effect of the oxygen is due to variations in the gas film on the glass surface resulting from the changes in the oxygen-pressure. If, however, the decomposition occurs mainly in the body of the gas, as appears from the work of Clarke and one of us (*loc. cit.*), the suggestion must for that reason alone be discarded.

Influence of Aqueous Vapour on the Rate of Decomposition of Ozone.

A second series of experiments was performed in order to investigate the influence of water vapour on the rate of decomposition of the gas—a subject of considerable interest, both on account of the diversity of the results obtained by previous workers and of its bearing on the general problem of the catalytic effect of moisture on most simple chemical changes.

The experiments were carried out as described above, except that both tubes were filled with ozonised oxygen at a pressure of a little less than an atmosphere, and that the gas which entered the tube A_1 was saturated with water vapour by its being passed through a small wash-bottle containing distilled water. To prevent any moisture being carried over into A_2, a tap was inserted on the left-hand side of the wash-bottle, which was shut off while A_2 was being filled.

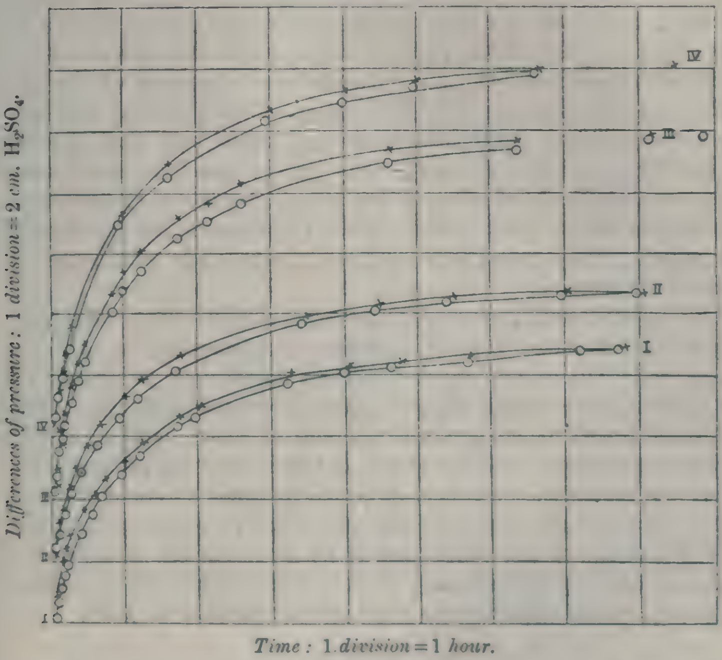
The eight curves obtained by plotting the results of four experiments are shown in Fig. 4. In experiments III*a* and IV*a*, the moist gas was contained in the tube which held the dry gas in the two previous experiments. The crosses correspond to the changes of pressure of the moist gas, and the circles to the changes of pressure of the gas dried by concentrated sulphuric acid.

Andrews and Tait, and also Brodie, in their classical memoirs on ozone, recommend the use of carefully dried oxygen for the preparation of ozone by the silent discharge.

Shenstone and Cundall (Trans., 1887, **51**, 610) showed that carefully dried oxygen can be easily converted into ozone—a fact which was shortly afterwards confirmed by Baker (Trans., 1894, **65**, 611), who stated that "ozone was formed as rapidly in oxygen dried with phosphorus pentoxide as it was in the same tube when the oxygen had been dried only by sulphuric acid."

As a result of further investigations, Shenstone (Trans., 1897, **71**, 471) drew the remarkable conclusion that all previous statements on the subject were wrong. He observed that a high percentage of ozone is formed by the action of the silent discharge on oxygen saturated with water vapour, and that the ozone thus produced is remarkably stable. On partly drying the gas, the percentage of ozone produced was considerably reduced, and the gas was found to be singularly unstable. Oxygen which had been thoroughly dried was found to become ozonised exceedingly badly. Subsequent investigations have failed to confirm Shenstone's work, and Armstrong has suggested that his anomalous results may be due to the presence of oxides of nitrogen (formed by continuous action of

FIG. 4.



the discharge from traces of nitrogen contained in the oxygen), which, as Andrews has shown, immediately destroy ozone.

Thomson and Threlfall (*Proc. Roy. Soc.*, 1885, **40**, 340) assert that ozone is produced when an electric spark is passed through very carefully dried oxygen.

Warburg (*loc. cit.*) maintains that at 100° the dry gas is just as stable as the moist.

Warburg and Leithäuser (*Ann. Physik*, 1906, [iv], **20**, 751) have, moreover, shown that the formation of ozone both in oxygen and in air is retarded by the presence of moisture, the retardation being greater in oxygen than in air.

Fischer and Marx (*Ber.*, 1906, **29**, 3631), working with a Nernst filament, find that the first traces of moisture lessen the yield of ozone by catalytic action, whereas larger quantities of water vapour increase the yield of hydrogen peroxide at the expense of the ozone.

Perman and Greaves (*loc. cit.*) claim to have shown that water vapour accelerates the decomposition of ozone, and that the effect is roughly proportional to the amount of water vapour present. They consider that the effect is due to the deposition of moisture on the surface of the glass, which causes the ozone to be more rapidly condensed. They point out that their results do not agree with those of Shenstone.

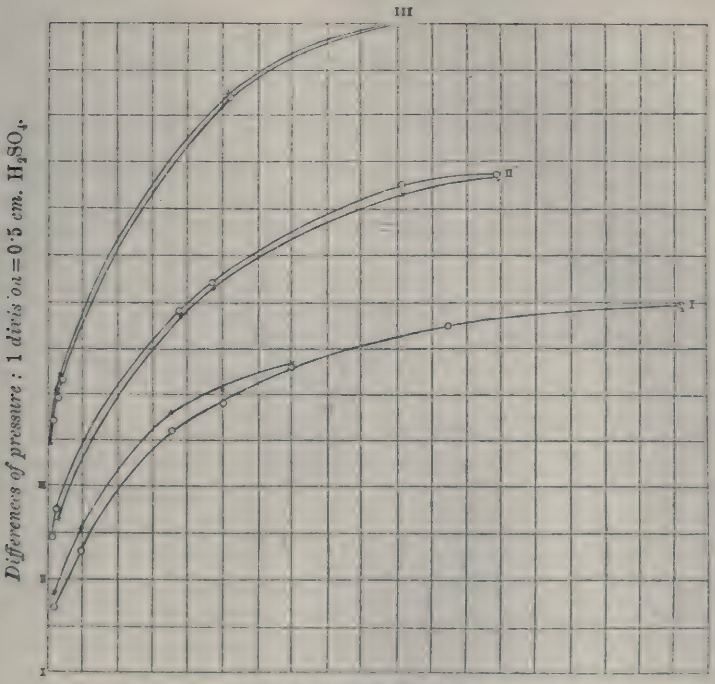
Although in our experiments the ozone mixed with a considerable proportion of water vapour appears to decompose at a slightly greater rate than that which has been dried with sulphuric acid, the difference is so small that we are disposed to think that it ought to be attributed to the gradual removal of water vapour, adsorbed on the inner surface of the glass, at the higher temperature, or to some similar cause. We are, at least, justified in concluding that at 100° a large difference in the quantity of water vapour present with the ozone is not accompanied by any marked change in the velocity of decomposition. Our results agree with those of Warburg, whose experiments were also conducted at 100°.

Influence of Nitrogen, Carbon Dioxide, Carbon Monoxide, and Chlorine on the Rate of Decomposition of Ozone.

The negative character of the results obtained with the first three gases is sufficient proof that no appreciable quantity of impurity capable of destroying the ozone was contained in them. In each case concentrated sulphuric acid was used to dry the gas. The experiments were conducted as follows.

A tube containing soda-lime was introduced between the gasholder and the ozone generator in order to remove any carbon dioxide from the oxygen. The tubes A_1 and A_2 were filled with ozonised oxygen at a pressure of half an atmosphere in the manner previously described. Oxygen was then admitted to one tube until a pressure slightly less than an atmosphere was registered by the manometer. The gas of which the effect was being investigated was then introduced into the other tube through T_1 or T_3 until the pressure in both tubes was the same. The rates of decomposition of the ozone in the two tubes were compared. Several experiments were performed, the gas under investigation being introduced into A_1 and A_2 alternately.

FIG. 5.

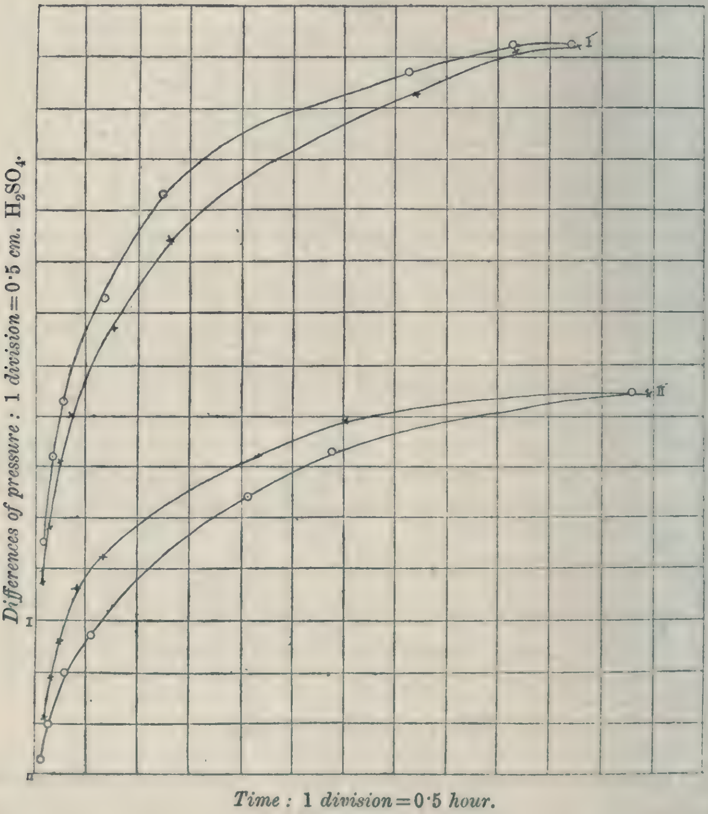


In the case of nitrogen, no effect on the velocity of decomposition was observed, while the experiments with carbon dioxide and carbon monoxide demonstrate that the influence, if any, of these gases is small. Chlorine, on the other hand, was found to decompose ozone so rapidly that it was quite impossible to make any trustworthy measurement of the velocity of decomposition.

The six curves obtained by plotting the results of three experiments with nitrogen are shown in Fig. 5. In the experiments II and III, the nitrogen was contained in the tube which in the previous experiment held ozonised oxygen only. The crosses correspond to changes of pressure in the gas which contained nitrogen, and the circles to the changes of pressure in the other tube.

The readings taken in the experiments with carbon dioxide I and carbon monoxide II are plotted in the curves shown in Fig. 6. The circles correspond to changes of pressure in the tube which contained the ozonised oxygen only.

FIG. 6.



Shenstone and Evans (Trans., 1898, **73**, 246), while investigating the influence of the silent discharge on atmospheric air, were surprised to find that as much as 98 per cent. of the oxygen contained in the air could be converted into ozone, the maximum yield of ozone obtained from pure oxygen under the same conditions being only 13·6 per cent. A similar observation was made by Brodie (*Phil. Trans.*, 1874, **164**, 101) when he submitted carbon dioxide to the action of the same agency; the carbon dioxide was decomposed into carbon monoxide and oxygen, 85 per cent. of the oxygen being in the form of ozone. It was conceivable that these interesting and peculiar phenomena might arise from inhibitive effects on the thermal decomposition of ozone of nitrogen and carbon dioxide respectively. The above experiments demonstrate that such an explanation is untenable, and that the phenomena in question must be due to some obscure influence of the nitrogen on the one hand, and the carbon dioxide or carbon monoxide on the other, on the energy of the discharge itself.

Observations on the Order of the Change.

In examining our results with a view to determining the order of the change, we have adopted a novel method. Instead of calculating the value of the constant for each observation on the assumption that the change is of a given order, we compare the amounts of ozone decomposed at given intervals of time with those calculated for changes of a specified order. This method of examining the results has the obvious advantage of enabling us to decide at a glance whether the departure of the experimental numbers from those calculated from any given set of assumptions as to the nature of the change lie within the limits of experimental error.

A curve of a given order is drawn through three points on the experimental curves, the points selected being the origin, and the points corresponding with the last observation, and an observation made when about half of the ozone was decomposed. The difference between the magnitudes of ordinates (amounts of ozone) of the experimental and calculated curve at different times are then tabulated. In the present case it was only necessary to compare the experimental curve with calculated curves drawn through it of the first and second order. It will be seen from the numbers given that the reaction is very nearly of the second order. Only the numbers obtained in those experiments in which large quantities of dry ozone were decomposed, and in which readings were taken for a considerable period of time are submitted to examination below.

*Examination of the Measurements Made in Experiment IV*a. (A_1.)

Time.	Observed change of pressure.	Calculated change of pressure, 1st order.	Difference: $k_1=0·00648$.	Observed change of pressure.	Calculated change of pressure, 2nd order.	Difference: $k_2=0·00142$.
2	0·60	0·36	+0·24	0·60	0·48	+0·12
5	1·30	0·91	+0·39	1·30	1·16	+0·14
10	1·90	1·68	+0·22	1·90	2·13	−0·23
16	2·95	2·57	+0·38	2·95	3·11	−0·16
58	7·00	7·00	0	7·00	7·00	0
97	8·50	9·26	+0·71	8·50	8·65	+0·10
178	10·30	11·26	+0·96	10·30	10·07	−0·23
238	10·95	11·76	+0·81	10·95	10·93	−0·02
298	11·40	11·97	+0·57	11·40	11·34	−0·06
397	11·85	12·08	+0·23	11·85	11·78	−0·07
508	12·10	12·10	0	12·10	12·10	0
		Sum of differences =	+4·51		Sum of differences =	−0·51

The calculated curves are drawn through the origin, the point (58, 7·00), and the point (508, 12·10). If the difference between the ordinates of the calculated and experimental curves indicates that the order of the reaction is of a higher value than that corresponding with the calculated curve, a plus sign is attached to it, a minus sign having the reverse significance.

It will be evident on inspection of the above numbers that the reaction differs but slightly from one of the second order.

*Examination of the Measurements made in Experiment III*a. (A_1.)

In this experiment the rate of change approximates still more closely to a reaction of the second order.

Time.	Observed change of pressure.	Calculated change of pressure, 1st order.	Difference: $k_1=0·00624$.	Observed change of pressure.	Calculated change of pressure, 2nd order.	Difference: $k_2=0·00141$.
1	0·25	0·17	+0·08	0·25	0·23	+0·02
3	0·75	0·50	+0·25	0·75	0·69	+0·06
6	1·55	0·95	+0·60	1·55	1·30	+0·25
9	1·95	1·44	+0·51	1·95	1·86	+0·09
12	2·40	1·88	+0·52	2·40	2·36	+0·04
18	3·15	2·69	+0·46	3·15	3·25	−0·10
24	3·85	3·26	+0·59	3·85	4·00	−0·15
30	4·50	4·15	+0·35	4·50	4·64	−0·14
51	6·10	6·16	−0·06	6·10	6·35	−0·25
60	6·85	6·85	0·00	6·85	6·85	0·00
75	7·50	7·82	+0·32	7·50	7·60	+0·10
105	8·60	9·24	+0·64	8·60	8·61	+0·01
129	9·15	10·00	+0·85	9·15	9·19	+0·04
156	9·75	10·60	+0·85	9·75	9·69	−0·06
276	11·00	11·63	+0·63	11·00	10·92	−0·08
381	11·40	11·81	+0·41	11·40	11·43	+0·03
489	11·80	11·85	+0·05	11·80	11·76	−0·04
531	11·85	11·85	0·00	11·85	11·85	0·00
		Sum of differences =	+7·06		Sum of differences =	−0·18

In the other experiments, in which the initial percentage of ozone was less, or the period during which observations were made shorter, the order of the change falls to a greater extent below the second. All the experiments are conclusive in demonstrating, however, that if the order of the change can be represented by an integral ordinal number, that number is the second.

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CCLV.—*The Colour Changes of Methyl-Orange and Methyl-Red in Acid Solution.*

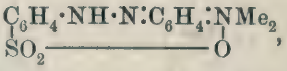
By Henry Thomas Tizard.

It is well known that the colour of an indicator in solution depends, within certain limits, on the concentration of the hydrogen ion (or hydroxyl ion) in the solution. These limits, which vary greatly with the nature of the indicator, have been determined for a large number of indicators by Fels (*Zeitsch. Elektrochem.*, 1904, **10**, 208) and Salessky (*ibid.*, p. 205), and a knowledge of them enables us to choose, for any given volumetric operation, the indicator that will give the best results. Conversely, by testing a solution with a large number of indicators, we can arrive at an estimate of the concentration of hydrogen ions in it. Friedenthal (*Zeitsch. Elektrochem.*, 1904, **10**, 114) and Salm (*Zeitsch. physikal. Chem.*, 1906, **57**, 471) have measured in this way the degree of dissociation of weak acids and weak bases, and have obtained results agreeing often to within a few per cent. of those obtained by conductivity measurements; but it can hardly be seriously proposed to supersede the latter, more accurate, although more laborious, method by the former, except when the acid or base under investigation is extremely weak. On the other hand, the determination of the degree of hydrolysis of salts in aqueous solution is often both laborious and at the same time subject to large percentage errors; a simple colorimetric method would therefore be of considerable importance, provided that it could be made as accurate as, or more so than, the methods usually employed. Friedenthal's method cannot be considered accurate enough for this purpose; the difficulty of judging colours without employing a suitable apparatus is very great, and, moreover, it is impossible to keep weakly acidic standard solutions of indicators (for comparison) unchanged for any length of time. It is far better to determine once and for all the relation between depth of colour and the concentration of the hydrogen ion.

For this purpose only those indicators can be used that are either colourless in one form, or exist in two coloured forms which are practically alike in tint and only differ in depth of colour. For all practical purposes, methyl-orange sufficiently fulfils the latter condition; the complete change of colour of this indicator from alkaline to strongly acid solutions can be followed by matching it against a suitable standard solution in a tintometer. I have therefore examined this change of colour with as great care and accuracy as possible, and have applied the results obtained to the determination of the hydrolysis of aniline salts at different dilutions (see following paper). Veley, in a series of papers (*Zeitsch. physikal. Chem.*, 1906, **57**, 147; Trans., 1907, and following years), has to a large extent opened up the field in this direction; but he worked only with extremely dilute solutions, where the total colour change is small, and the error of observation relatively large. Further, he based all his conclusions on empirical relations, which can be only approximately true. For these and other reasons, which will be mentioned later, his results can only be considered qualitative.

Theory of the Colour Change.

The simplest theory of the colour changes of an indicator is that of Ostwald. According to this, the ions of an indicator have a different colour from that of the undissociated molecule. For example, the undissociated molecule, $NMe_2\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot SO_3H$, is red, whilst the ion, $NMe_2\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot SO_3'$, is light yellow. It has recently been proved in many cases, and is probably true in all, that this change in ionisation is accompanied by a change in the chemical structure of the molecule. According to Hewitt, the undissociated molecule of methyl-orange mainly consists of an internal compound,



$$\begin{array}{l} C_6H_4\cdot NH\cdot N{:}C_6H_4{:}NMe_2 \\ SO_2 \text{———————} O \end{array},$$

to which the deep red colour is due. From this point of view, indicators are pseudo-acids, the pseudo-acidic form being always in equilibrium with the true acidic form, from which the ions are directly derived. It must, however, be emphasised that these considerations make no difference whatever to the theoretical treatment from the ionic point of view; for if the undissociated acid exists in solution in two or even more forms, these must always be present in strictly constant ratios, and hence, for all practical purposes, the acid behaves as if it existed in only one form. This will be assumed to be true for the sake of clearness in the following considerations, but it must be understood that the results obtained have no bearing on the question as to what particular form of the undissociated molecule the deep red colour is due.

Now let the molecular colour of the ion be taken as unity, and let that of the undissociated acid be equal to c_1. By this we mean that if the colour of a solution containing completely dissociated methyl-orange is balanced by a height "h" of a standard solution in a tintometer, the colour of the same solution when excess of acid (hydrochloric) is added, that is, when the indicator is entirely in the undissociated form, will be balanced by a height $= c_1 \times h$.

Then the molecular colour of a solution containing methyl-orange partly in the undissociated form, and partly in the form of ions, will be somewhere between c_1 and 1. Let y equal the fraction undissociated, and therefore $(1-y)$ the fraction dissociated. The molecular colour of the solution is then obviously given by the equation:

$$C = c_1 y + (1 - y) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

Further, if K_a is the dissociation constant of the indicator acid, we have by Ostwald's law:

$$K_a y = (1 - y) \times \text{conc. H}^{\cdot} \quad . \quad . \quad . \quad . \quad (2).$$

Eliminating y from (1) and (2), we have:

$$\text{conc. H}^{\cdot} = K_a \frac{C - 1}{c_1 - C} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

Hence, if we know K_a and c_1, the relation between the molecular colour C of a solution and the concentration of hydrogen ions it contains is completely determined. K_a and c_1 can be determined by measuring the colour of solutions containing varying quantities of hydrochloric acid.

When $y = 1/2$, that is, when the indicator acid is 50 per cent. dissociated, the molecular colour:

$$C = \frac{c_1 + 1}{2},$$

that is, is just midway between the two extreme colours.

Further, equation (2) becomes:

$$K_a = \text{conc. H}^{\cdot}.$$

In a solution, therefore, the colour of which is just midway between the two extreme colours, the concentration of the hydrogen ion is equal to the dissociation constant of the indicator acid. Salm (*loc. cit.*) has determined in this way the dissociation constant of a large number of indicators. He measured the concentration of the hydrogen ions by means of a hydrogen electrode. The method is of advantage when the two extreme colours of an indicator differ widely, but since only one solution can be conveniently examined, the results are probably not very accurate, although of the right order of magnitude.

Now there is another point with regard to methyl-orange and allied indicators which has not been taken into account in the above considerations. All these compounds contain a substituted amino-group, and are therefore amphoteric electrolytes. Hence in an acid solution the basic ion, for example,

$$\dot{\mathrm{N}}\mathrm{HMe_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}SO_3H},$$

may be present, as well as the undissociated molecules. To this basic ion we must assign a molecular colour, say c_2, and its presence to any considerable extent would greatly affect conclusions drawn from colour measurements. Lundén has, in fact, criticised Veley's results adversely from this point of view, but, as will be shown later, the basic dissociation constant K_b of methyl-orange is so small that no appreciable quantity of the $\mathrm{H\dot{N}Me_2R}$ ion is formed even in $N/20$-hydrochloric acid. On the other hand, that of methyl-red (which differs from methyl-orange in having an ortho-carboxyl instead of a para-sulphonic group) is larger, and in consequence we find that the basic properties of this indicator have a considerable influence on the colour in solutions which are greater than $N/5000$ with respect to hydrogen ions.

If we consider solutions which contain only the basic ion and the undissociated acid, and if the fraction of the former present is y', and therefore that of the latter is $(1-y')$, then as before:

$$C = c_2y' + c_1(1-y') \quad . \quad . \quad . \quad . \quad . \quad (1a).$$

Also, Ostwald's law gives:

$$K_b(1-y') = y' \times \text{conc. OH}'.$$

Since

$$\text{conc. OH}' = \frac{K_w}{\text{conc. H}^{\cdot}}$$

(K_w = dissociation constant of water), the last equation becomes:

$$\frac{K_w}{K_b}.y' = (1-y') \times \text{conc. H}^{\cdot} \quad . \quad . \quad . \quad . \quad (2a).$$

These two equations are precisely similar in form to equations (1) and (2), and it is evident that we cannot decide at once, without further evidence, whether the "dissociation constant," found colorimetrically, of an amphoteric indicator is really K_a or $\frac{K_w}{K_b}$. This is especially true when the dissociation constant is found by Salm's method. When the whole course of the colour curve is examined, it is generally possible to see at a glance whether the change of colour must be attributed to the presence of three coloured molecules (basic ion, undissociated molecule, acid ion) in the solution, or only two (compare the curves for methyl-red and methyl-orange).

EXPERIMENTAL.

To test these equations, and to determine the values of K_a and c_1, the depth of colour of methyl-orange solutions of known strength in presence of hydrochloric acid ranging from *N*/20- to *N*/100,000 has been investigated. The apparatus employed was the Donnan tintometer, used as described, for example, by Sidgwick and Tizard (Trans., 1908, **93**, 188). The standard used for comparison was a faintly acid solution of methyl-orange. It was, of course, unnecessary to know its exact strength, as it was compared before any series of measurements against a neutral solution of methyl-orange of known strength. The colours were all referred to this dilution as unit. Veley (*loc. cit.*) found it impossible to measure the depth of colour of a strongly acid (red) solution of methyl-orange by comparing it to the same standard that he used in his colour measurements with weakly acidic (orange) solutions. I found comparatively little difficulty in doing so; the difference may be partly due to the fact that whilst Veley used daylight as his illuminant, I used the yellow light from a 50 c.p. electric lamp (carbon filament).

All the solutions used were made up carefully by weight with conductivity water. They were filtered to remove dust as far as possible, and kept in steamed-out Jena-glass flasks.

It was found impossible to prepare a clear solution of methyl-orange with a concentration greater than *N*/1000. In fact, solutions of this strength were slightly turbid, but immediately cleared on dilution. The effect of dilution is to cause a slight decrease in molecular colour, as the following measurements show.

Ten c.c. of a neutral solution, *N*/2000, were taken and diluted in the tintometer tube.

		V for methyl-orange.	Height of balancing column.
10 c.c. *N*/2000 solution	....	2000	4·6
,, ,, ,,	+10 c.c. H_2O	4000	4·3
,, ,, ,,	+20 c.c. H_2O	8000	4·0
,, ,, ,,	+60 c.c. H_2O	20,000	4·0
,, ,, ,,	+a few drops *N*/10-alkali	20,000	4·0

This decrease in colour may be due to increasing dissociation; the presence of even a small quantity of undissociated salt may have a considerable effect on the colour. In the experiments with hydrochloric acid, the methyl-orange was used at a dilution of $V = 20{,}000$, high enough to avoid complications of this kind. The last colour measurement is important. Methyl-orange is a sodium salt; if its corresponding acid were very weak, the salt would be considerably hydrolysed at high dilutions. This means that the solution would contain undissociated acid, which is of a much deeper colour than its ions. Addition of alkali would, in this case, diminish the colour by destroying hydrolysis. As a matter of fact, no such effect is observed, and this is strong evidence that the acid of methyl-orange cannot be very weak; on the contrary, it must be considerably stronger than acetic acid. We should therefore expect its basic dissociation constant, K_b, to be correspondingly small. These conclusions are confirmed by the colour measurements with hydrochloric acid. The latter measurements were carried out in the following way. Ten to 50 c.c. of an $N/10{,}000$-solution of methyl-orange were placed in the tintometer tube, a suitable quantity of a standard solution of hydrochloric acid added, and then water added up to twice the original volume of methyl-orange. The concentration of the latter was then $N/20{,}000$. That of the hydrochloric acid varied from $N/20$ to $N/100{,}000$; or, if we denote the ratio (mols. HCl) ÷ (mols. methyl-orange) by "*a*," "*a*" varied from $20{,}000 \div 100{,}000 = 0{\cdot}2$ to $20{,}000 \div 20 = 1000$.

If the height of the balancing column is h', and the height required to balance the same amount of methyl-orange in neutral solution is h, then the molecular colour of the acid solution is given by:

$$C = \frac{h'}{h},$$

that of the neutral solution being taken as unity.

Three series of measurements were taken on different days, and with entirely fresh solutions. The temperature was 25°. The greatest deviation in the molecular colour found for any particular strength of solution was 5 per cent., the usual error being 2 to 3 per cent.. It was found impossible to reduce the error consistently beyond this point.

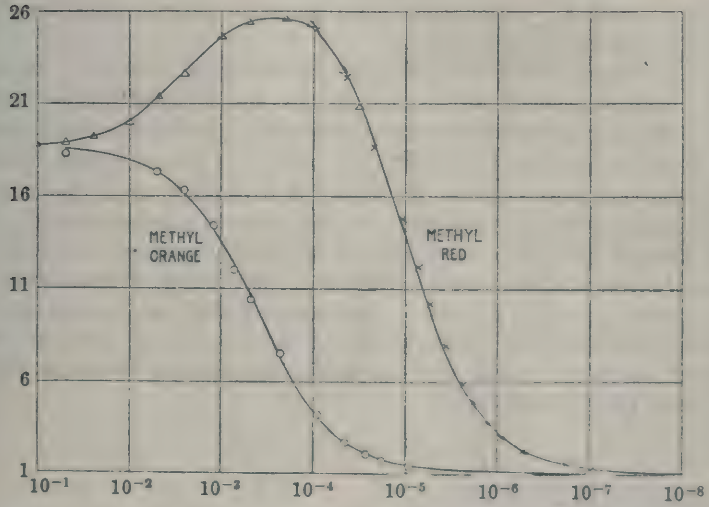
The curve for methyl-orange is drawn by plotting molecular colour against concentration of hydrogen ions, the latter being expressed in inverse powers of 10. There is very little change in colour between $H^{\cdot}$ concentrations of 10^{-7} (neutral solution) and 10^{-5}; after this point the rise in colour is rapid—the middle part of the curve being practically a straight line—until a maximum is reached somewhere about the point conc. $H^{\cdot} = 10^{-2}$, the colour only rising about 5 per cent. in more concentrated solutions. It is obvious from the curve that these changes can be explained if we assume the presence of two coloured substances in the solution. These must evidently be the anion and the undissociated acid, and equations (1) and (2), or (3) may therefore be applied.

The concentration of hydrogen ions in the solutions examined is, however, by no means the same as that of the hydrochloric acid added, as Veley assumed, since the undissociated indicator acid in the solution is formed by a combination of part of the anion of the salt with hydrogen ions derived from the added hydrochloric acid. In other words, the concentration of hydrogen ion in the solution is not a/V, where V is the dilution of methyl-orange, but

$$\frac{a-y}{V},$$

y being the fraction present in the form of undissociated indicator acid.

This correction is of considerable importance, especially at the



extreme dilutions with which Veley worked, and the fact that he did not take it into account may possibly explain some of his anomalous conclusions.

Equation (2) may therefore be written in the form:

$$K_a.V.y = (1-y)(a-y),$$

where $V = 20{,}000$.

From the results, the mean values for K_a and c_1 are found to be:

$$K_a = 4{\cdot}25 \times 10^{-4} \text{ (at } 25^\circ\text{)}.$$
$$c_1 = 18{\cdot}8.$$

The agreement between calculated and observed values is shown in the following table:

$a = \frac{\text{mols. HCl}}{\text{mols. indicator}}$.	Conc. $H^{\bullet} = \frac{a-y}{20,000}$.	y.	Colour (calc.).	Colour (obs.).
0·0	10^{-7}*	0·00	(1·00)	(1·00)
0·2	$10^{-5·048}$	0·021	1·37	1·38
0·4	$10^{-4·746}$	0·041	1·73	1·68
0·6	$10^{-4·568}$	0·060	2·07	2·04
0·8	$10^{-4·443}$	0·078	2·39	2·39
1·0	$10^{-4·344}$	0·096	2·71	2·65
2·0	$10^{-4·040}$	0·177	4·15	4·18
5·0	$10^{-3·634}$	0·353	7·28	7·48
10·0	$10^{-3·324}$	0·527	10·4	10·7
15·0	$10^{-3·144}$	0·63	12·2	12·0
25·0	$10^{-2·916}$	0·74	14·2	14·4
50·0	$10^{-2·609}$	0·85	16·1	16·3
100·0	$10^{-2·305}$	0·92	17·4	17·3
1000·0	$10^{-1·300}$	0·99	18·6	18·3

* Neutral point.

Salm found $K_a = 4·6 \times 10^{-4}$ as a mean of several values ranging from 4·0 to 5·5.

The greatest deviation between the observed molecular colours and those calculated by means of the above equations is 3 per cent. It appears therefore that there is no appreciable quantity of the positive ion $\overset{\bullet}{N}Me_2R$ formed even when the concentration of the hydrogen ion is as high as $N/20$, for it is unlikely that the colour of this ion is the same as that of the undissociated molecule. In the parallel case of methyl-red, it is distinctly lower, as will be shown later. If we assume that not more than 1 per cent. of the methyl-orange is present in the form of the basic ion when the concentration of the hydrogen ion in the solution is 10^{-2}, we can deduce an upper limit for the basic dissociation constant from equation (2a), which gives:

$$\frac{K_w}{K_b} \times 0·01 = 0·99 \times 10^{-2},$$

or $K_b = K_w = 10^{-14}$ (at 25°).

K_b is therefore probably $< 10^{-14}$.

When a is greater than 1, the increase in colour is approximately proportional to the increase in the amount of hydrochloric acid in the solution. Thus, with each successive 0·2 molecule, the increase in colour (calculated) is 0·37, 0·36, 0·34, 0·32, 0·32. This agrees with the observations of Veley, who found that by plotting increase in colour against concentration of acid added, a straight line was obtained. The relation is, however, evidently only approximately true.

At the theoretical neutral point the concentration of hydrogen ions is 10^{-7}. Since methyl-orange does not appreciably lighten in colour below a concentration of $H^{\bullet} = 10^{-5}$, it must be considered a bad indicator for accurate volumetric analysis, apart from the fact that, since the change of colour takes place only gradually, it is difficult to get a sharp end-point. On the other hand, the closeness of the results obtained with those required by the simple theory expressed by equations (1) and (2) shows that methyl-orange is a very good indicator to use for the quantitative colorimetric estimation of the concentration of hydrogen ions between 10^{-3} and 10^{-5}, that is, between $N/1000$ and $N/100,000$.

Substituting the values found for K_a and c_1 in (3), we get for the relation between concentration of hydrogen ions and molecular colour of methyl-orange the expression:

$$\text{conc. H}^{\cdot} = 4{\cdot}25 \times 10^{-4}.\frac{C-1}{18{\cdot}8-C}.$$

Methyl-red.

In order to throw further light on the colour changes of indicators which are amphoteric electrolytes, a series of similar colour measurements were made with methyl-red, an indicator discovered by Rupp and Loose (*Ber.*, 1908, **41**, 3905). Its constitution is expressed by the formula:

$$NMe_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CO_2H\ (o).$$

The method of preparation given by these authors is not satisfactory, only small yields being obtainable. The following method is recommended by Mr. T. F. Winmill, who kindly supplied me with the indicator in the first place.

Five grams of anthranilic acid are dissolved in 150 c.c. of water and 15 c.c. of concentrated hydrochloric acid. To this, 2·5 grams of solid sodium nitrite are added, and the solution kept for half an hour. It is then poured into a solution of 4·65 grams of dimethylaniline in a mixture of 5 c.c. of concentrated hydrochloric acid and 50 c.c. of water. Fifty grams of sodium acetate are added. On warming to 40°, the red product quickly separates, but the reaction does not appear to be complete for about three hours. The substance is then collected, and can be crystallised from glacial acetic acid. The yield is almost quantitative.

Methyl-red is very insoluble in water; its saturated solution at the ordinary temperature is only about $N/100,000$. Since it contains a carboxyl instead of a sulphonic group, we should expect it to be a weaker acid than methyl-orange, and a correspondingly stronger base. In accordance with this, methyl-red is easily soluble both in acids and in alkalis. Its alkali salts are surprisingly soluble; the potassium salt can only be obtained by evaporating an alcoholic solution to dryness, since it is soluble to a considerable extent in ether, and deliquescent in air. Since the sodium salt of helianthin (methyl-orange) is somewhat insoluble in water, the difference in behaviour is striking.

The pure potassium salt appears to dissolve completely in a very small quantity of water, forming a very deep red solution; on diluting further, the acid separates out. The hydrolysis appears to be excessive if we accept the value for the dissociation constant of the acid (10^{-5}), found from the colour measurements, but since the solubility of the acid is so small, the appearance may be deceptive. It would probably be interesting to investigate further the behaviour of the alkaline salts of this indicator, but this does not come within the scope of the present paper.

Since a clear neutral solution of the salt could not be obtained, the saturated solution of the acid was used in the colour measurements. Its strength was found approximately in the following way. A known quantity of the potassium salt was dissolved in a slight excess of alkali, so as to make an $N/1000$-solution; 10 c.c. of this were then diluted to 1 litre. This $N/100,000$-solution contained, of course, a slight, but only a slight, excess of alkali. Ten c.c. were placed in the tintometer tube, the same volume of $N/1000$-hydrochloric acid added, and the colour was measured. Ten c.c. of the saturated solution of the acid + 10 c.c. of $N/1000$-hydrochloric acid were then measured in the same way. It makes no difference if the concentration of hydrogen ions in this solution was slightly greater than that in the salt solution, for, as will be shown later, the molecular colour is at a maximum at this point, and does not change appreciably between $H^{\cdot}$ concentrations of $N/5000$ and $N/2000$ (see the curve for methyl-red).

Since the depth of colour of the two solutions was approximately the same, the strength of the acid solution was taken to be roughly the same as that of the salt solution, namely, $N/100,000$. The saturated solution was usually diluted in the tube up to about four times its original volume.

It has already been pointed out in discussing the results with methyl-orange, that the concentration of the hydrogen ions in a very dilute solution of hydrochloric acid containing an indicator, is not the same as that of the hydrochloric acid itself, but is less or greater, as the case may be. In order to allow properly for this, we must, of course, know exactly the quantity of indicator present. The uncertainty of the actual dilution of the methyl-red used makes, therefore, experiments with hydrochloric acid untrustworthy when the concentration of the latter falls below a certain amount. For this reason, the most dilute solution of hydrochloric acid used was about $N/30,000$, and the concentration of the hydrogen ion in this and more concentrated solutions was taken to be the same as that of the hydrochloric acid present. The remainder of the curve was determined by measuring the colour in solutions of sodium acetate containing varying amounts of acetic acid. The concentration of the sodium acetate was $N/500$; that of the hydrogen ions, when a certain amount of acetic acid, equal to n times that of the sodium acetate, is added, may then be easily calculated by means of Ostwald's law, the dissociation constant of acetic acid at 18° (the temperature of measurement) being taken as $1{\cdot}8 \times 10^{-5}$. Hence:

$$1{\cdot}8 \times 10^{-5} \times \text{conc. HA} = \text{conc. A}' \times \text{conc. H}^{\bullet}.$$

Since we may assume the sodium acetate to be completely dissociated, the equation becomes:

$$\begin{aligned}\text{conc. H}^{\bullet} &= 1{\cdot}8 \times 10^{-5} \times \frac{\text{HA}}{\text{NaA}}.\\ &= n \times 1{\cdot}8 \times 10^{-5}.\end{aligned}$$

Since the amounts of acetic acid and sodium acetate in the solution are always large compared to that of the indicator, the correction that must be made when strong acids, such as hydrochloric acid, are used is unnecessary.

The colour curve obtained in this way is shown on p. 2483. The lower part of the curve is similar to that of methyl-orange, but the colour falls again when the concentration of hydrogen ions is greater than $N/2000$ or thereabouts. We must therefore assume that two changes take place:

$$\text{I. } \text{NMe}_2 \ldots \text{COO}' + \text{H}^{\bullet} \rightleftharpoons \text{NMe}_2 \ldots \text{CO}_2\text{H}.$$
$$\text{II. } \text{NMe}_2 \ldots \text{CO}_2\text{H} + \text{H}^{\bullet} \rightleftharpoons \dot{\text{N}}\text{HMe}_2 \ldots \text{CO}_2\text{H}.$$

The colours of the acid ion, undissociated molecule, and basic ion are taken, as before, as 1, c_1, and c_2 respectively. Since the maximum is very flat, the first change must be nearly complete before the second begins. Disregarding the latter for the present, then, we may apply the equations:

$$\begin{aligned}C' &= c_1 y + (1 - y),\\ K'_a y &= (1 - y) \times \text{conc. H}^{\bullet},\end{aligned}$$

to the lower part of the curve, the concentration of hydrogen ions being calculated in the ways already indicated. For the mean values of K'_a and c_1, we find:

$$\begin{aligned}K'_a &= 1{\cdot}05 \times 10^{-5}.\\ c_1 &= 27{\cdot}6.\end{aligned}$$

The temperature was in this case 18°.

The following table contains the results so obtained:

Molecular Colour of Methyl-red.

1.—*Experiments with Mixtures of Sodium Acetate and Acetic Acid.*

$n=\frac{HA}{NaA}$.	Conc. $H^{\cdot}$.	Colour (obs.).	Colour (calc.).
0·0	$10^{-8\cdot272}$	1·10	1·02
0·005	$10^{-7\cdot046}$	1·26	1·22
0·01	$10^{-6\cdot745}$	1·46	1·46
0·03	$10^{-6\cdot268}$	2·24	2·30
0·05	$10^{-6\cdot046}$	3·00	3·10
0·07	$10^{-5\cdot900}$	3·68	3·84
0·1	$10^{-5\cdot745}$	4·86	4·88
0·13	$10^{-5\cdot631}$	5·86	5·84
0·2	$10^{-5\cdot444}$	7·84	7·78
0·3	$10^{-5\cdot268}$	10·2	10·2
0·4	$10^{-5\cdot143}$	12·2	11·8
0·6	$10^{-4\cdot967}$	14·8	14·5
1·2	$10^{-4\cdot666}$	18·6	18·9
2·4	$10^{-4\cdot365}$	22·0	22·4
5·0	$10^{-4\cdot046}$	25·2	24·8

2.—*Experiments with Hydrochloric Acid up to* N/2000.

V_{HCl}.	Conc. $H^{\cdot}$.	Colour (obs.).	Colour (calc.).
31,000	$10^{-4\cdot491}$	19·9	21·0
21,000	$10^{-4\cdot322}$	22·3	22·8
11,000	$10^{-4\cdot041}$	24·9	24·8
9000	$10^{-3\cdot954}$	25·4	25·3
[5000	$10^{-3\cdot699}$	25·6	26·2]
[2000	$10^{-3\cdot301}$	25·6	27·0]

The observed and calculated values closely agree; in particular the two series of measurements agree well where they overlap. The last colour measurement (in $N/2000$-hydrochloric acid) is considerably below the calculated value; this is due to the formation of the basic ion. In still higher concentrations of hydrogen ions, the colour sinks further, until it again becomes practically constant when conc. $H^{\cdot}$ is greater than $N/20$. Equations (1*a*) and (2*a*) apply to this case. If we assume that no acid dissociation takes place, we get:

$$C=y_2c_2+(1-y_2)c_1,$$

where y_2 is the fraction of the indicator present in the basic form, and c_2 is the molecular colour of the basic ion; c_1 has already been found to be 27·6.

Also, if K_b is the basic dissociation constant of the indicator:

$$\frac{K_w}{K_b}y_2=(1-y_2)\text{ conc. }H^{\cdot}.$$

From the colour measurements, we find:

$$\frac{K_w}{K_b}=2\cdot0\times10^{-3}.$$

$$c_2=18\cdot6.$$

Molecular Colour of Methyl-red in Solutions of Hydrochloric Acid greater than N/5000.

V_{HCl}.	Conc. H˙.	Colour (obs.).	Colour (calc.).
2	$10^{-0\cdot 3}$	18·4	18·6
10	$10^{-1\cdot 0}$	18·8	18·8
20	$10^{-1\cdot 3}$	18·8	18·9
30	$10^{-1\cdot 5}$	18·9	19·1
40	$10^{-1\cdot 60}$	19·2	19·2
100	$10^{-2\cdot 00}$	19·9	20·0
210	$10^{-2\cdot 322}$	21·6	21·4
410	$10^{-2\cdot 613}$	23·0	22·6
1000	$10^{-3\cdot 00}$	24·8	24·6
[2000	$10^{-3\cdot 301}$	25·6	25·8]
[5000	$10^{-3\cdot 699}$	25·6	26·7]

The dilutions $V_{HCl} = 2000$ and 5000 require further consideration; it is evident that the molecular colours at and between these dilutions cannot strictly be calculated on either of the assumptions: (1) that no basic ion is present, (2) that no acid ion is present. Both these ions as well as the undissociated molecule must be present to an appreciable extent. By using the dissociation constants given above, we can calculate the amount of these ions present, and thus arrive at the following results:

V_{HCl}.	Acid ion. $(1 - y_1 - y_2)$	Undiss. mol. y_1	Basic ion. y_2	Col. (calc.).	Col. (obs.).
2000	0·015	0·788	0·197	25·4	25·6
5000	0·045	0·868	0·087	25·6	25·6

Hence the whole course of the colour curve is satisfactorily accounted for.

Since $K_w = 0\cdot 6 \times 10^{-14}$ at 18°,

we have
$$K_b = \frac{0\cdot 6 \times 10^{-14}}{2 \times 10^{-3}} = 3 \times 10^{-12}.$$

It must not, of course, be assumed that the colours of methyl-orange and methyl-red are the same in equivalent alkaline solution, because the molecular colours of both the acid ions have been taken as unity. As a matter of interest, however, it may be mentioned that, as far as could be judged, the difference between the two depths of colour of the two acid ions is but small.

As an indicator methyl-red is greatly superior to methyl-orange, as the colour curves show. The visible change, red to yellow, takes place between $10^{-5\cdot 7}$ and 10^{-7}, that is, between H˙ concentrations of *N*/200,000 and *N*/10,000,000. Not only therefore is the end-point very much sharper than when methyl-orange is used, but the neutral point so found is very much nearer the theoretical neutral point. Methyl-red is, in fact, an extremely sensitive indicator, and should come into extended use; it is especially valuable for the exact titration of moderately weak bases (such as ammonia) by strong acids.

As a means for measuring colorimetrically the concentration of hydrogen ions in a solution, methyl-red would probably be found valuable when such concentration lies between 10^{-5} and 10^{-6}. Methyl-orange cannot be used when conc. $H^{\cdot}$ is greater than 10^{-5}. If methyl-red is used for this purpose, it would be advisable to refer all molecular colours to the maximum colour found when conc. $H^{\cdot}$ lies between $N/2000$ and $N/5000$; this maximum colour can be measured very accurately, whilst the extreme yellow colour of the ion is somewhat difficult to measure. Taking the maximum colour as 25·6, the theoretical colour of the undissociated molecule is 27·6, and the relation between concentration of hydrogen ions (between $10^{-4\cdot5}$ and $10^{-6\cdot5}$, say) and the molecular colour of the solution can be expresed by the equation:

$$\text{conc. } H^{\cdot} = \frac{1{\cdot}05 \times 10^{-5}(C-1)}{27{\cdot}6 - C}.$$

Summary.

The depths of colour of methyl-orange and methyl-red in solutions of varying concentrations of hydrogen ions have been measured.

From the results, the following constants have been deduced:

	K_a.	K_b.
Methyl-orange (at 25°):		
$NMe_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}SO_3H$ ………	$4{\cdot}25 \times 10^{-4}$	$< 10^{-14}$
Methyl-red (at 18°):		
$NMe_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CO_2H$ (*o*) ……	$1{\cdot}05 \times 10^{-5}$	3×10^{-13}

The value of methyl-red as an indicator is discussed.

Expressions are given connecting the depths of colour of methyl-orange and methyl-red solutions with the concentrations of hydrogen ion in the solutions.

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CCLVI.—*The Hydrolysis of Aniline Salts Measured Colorimetrically.*

By HENRY THOMAS TIZARD.

IN the preceding paper it was shown that the concentration of hydrogen ions in a solution of methyl-orange, the molecular colour of which is C, is given by the equations:

$$C = 18{\cdot}8y + (1-y) \quad \ldots\ldots\ldots\ldots \quad (1)$$
$$4{\cdot}25 \times 10^{-4}y = (1-y) \times \text{conc. } H^{\cdot} \quad \ldots\ldots\ldots \quad (2),$$

where y denotes the fraction of methyl-orange present in the form of undissociated indicator acid.

These equations have now been used to determine colorimetrically the degree of hydrolysis of aniline salts.

Aniline Hydrochloride.

Aniline hydrochloride was prepared by mixing equivalent quantities of pure concentrated hydrochloric acid and aniline, which was purified in the way recommended by Hantzsch and Freese (*Ber.*, 1894, **27**, 2966). The salt was recrystallised from water slightly acidified with hydrochloric acid. The colour measurements were made in exactly the same way as that described in the preceding paper. The temperature of observation was 25°. One of the chief objections to the measurement of hydrolysis by colorimetric observations seems to be the difficulty of keeping the temperature constant. It was found best to keep the solutions until just before use in a thermostat at the required temperature, and then to transfer the requisite amount quickly to the tintometer tube. Since with a certain amount of practice accurate colour measurements can be made very rapidly, the temperature alters only slightly during the actual experiment. In the experiments communicated in this paper, it certainly did not vary sufficiently to affect the colour outside the unavoidable error of observation.

The dilutions examined ranged from 1/20- to 1/1200-normal.

In a pure aqueous solution of a salt of a weak base, the concentration of the hydrolysed base is, of course, equal to that of the free hydrogen ions in the solution. When, however, an indicator, such as methyl-orange, is also present in the solution, it partly combines with the hydrogen ions, and the concentration of the latter will therefore be less than that of the hydrolysed base. Thus, if x is the fraction of salt hydrolysed, V_1 the dilution of the salt, V_2 that of the indicator, and y (as before) the fraction of the latter present in the form of undissociated acid:

$$\frac{x}{V_1} = \text{conc. aniline}$$
$$= \text{conc. H}^{\cdot} + \frac{y}{V_2}.$$

This correction is of considerable importance when hydrolysis is large and the dilution of the indicator not too great. Thus, to take an example from the following table, when $V_1 = 200$ and $V_2 = 20{,}000$, the molecular colour is found to be 8·63. From equations (1) and (2) we get:

$$y = 0{\cdot}429, \text{ conc. H}^{\cdot} = 3{\cdot}19 \times 10^{-4};$$

hence

$$\text{conc. aniline} = 3{\cdot}19 \times 10^{-4} + \frac{0{\cdot}429}{20{,}000}$$
$$= 3{\cdot}40 \times 10^{-4}.$$

The difference between the two concentrations is thus 7 per cent. It was not taken into account by Veley in researches of a similar nature, and this, together with the reasons already put forward in the previous paper, may explain the frequent difference between his results and those arrived at by other methods.

The hydrolysis constant is given by the equations:

$$\frac{K_w}{K_b} = \frac{\text{conc. } C_6H_5{\cdot}NH_2 \times \text{conc. } H^{\bullet}}{\text{conc. } C_6H_5{\cdot}NH_3} = \frac{x}{1-x} \times \text{conc. } H^{\bullet}.$$

The following table contains the results obtained:

V_1.	V_2.	Colour (C).	$y=\frac{C-1}{17{\cdot}8}$.	conc. $H^{\bullet} \times 10^4$.	$100x$.	$\frac{K_w}{K_b} \times 10^4$.
20	20,000	12·6	0·652	7·94	1·65	(0·133)
30	30,000	11·9	0·612	6·71	2·07	(0·142)
40	40,000	11·4	0·584	5·97	2·51	(0·154)
60	30,000	10·7	0·545	5·09	3·16	(0·176)
80	20,000	10·4	0·528	4·76	4·12	(0·204)
100	30,000	9·86	0·498	4·21	4·38	(0·193)
200	20,000	8·63	0·429	3·19	6·80	0·230
300	15,000	7·84	0·384	2·65	8·73	0·253
400	20,000	6·97	0·335	2·14	9·24	0·218
500	20,000	6·63	0·316	1·96	10·6	0·232
600	15,000	6·25	0·295	1·78	11·9	0·240
800	13,333	5·86	0·273	1·59	14·3	0·265
1000	20,000	5·48	0·252	1·43	15·6	0·264
1200	20,000	4·92	0·220	1·20	15·7	0·223

A 2 per cent. error in colour measurement corresponds on an average with an error in the hydrolysis constant of 10 per cent., so that the fluctuations of the constant from the mean value for the last eight dilutions are within the error of observations, and, moreover, are not materially greater than those found when other methods of measurement are employed. The actual mean value of the constant for these eight dilutions is:

$$\frac{K_w}{K_b} = 0{\cdot}242 \times 10^{-4},$$

whereas Bredig (*Zeitsch. physikal. Chem.*, 1894, **13**, 239) found by conductivity measurements:

$$\frac{K_w}{K_b} = 0{\cdot}24 \times 10^{-4}.$$

The two values are thus practically identical.

At higher concentrations, however, the constant is very much smaller, and appears to increase quite regularly with the dilution. This difference is too great to be accounted for by the incomplete dissociation of the aniline hydrochloride, and as the behaviour has not been observed when other methods are used, it is presumably due to the formation of a compound with methyl-orange, which affects the colour to a small extent. With aniline acetate, however, no such phenomenon was observed; the colour in a $N/20$-solution of this salt is perfectly normal. The so-called neutral salt action discussed by Szyszkowski (*Zeitsch. physikal. Chem.*, 1910, **73**, 269) is apparently unconnected with the above phenomenon, for methyl-orange appears to indicate a higher concentration of hydrogen ion in presence of sodium chloride than the solution contains, whereas the reverse is true with aniline hydrochloride.

On the whole, it is perhaps inadvisable to use concentrated solutions of salts in colour measurements of this kind.

Aniline Acetate.

This salt has apparently not been prepared in the solid state. A mixture of equivalent weights of pure aniline and acetic acid will not solidify when cooled to $-20°$, but as the liquid is extremely viscous at this temperature, it is probably supercooled. If the equivalent mixture is kept for some time, acetanilide is formed. The solution used in these experiments was therefore made by mixing equivalent quantities of $N/5$-aniline and $N/5$-acetic acid, both of which were made up accurately by weight from the pure substances.

In a solution of a salt of a weak acid and a weak base, the dissociation constants of which are K_a and K_b respectively, let γ be the degree of dissociation of the salt, and x the fraction hydrolysed; then Ostwald's law gives the two equations:

$$K_a.x = (1 - x) \times \text{conc. H}^{\cdot}$$
$$K_b.x = (1 - x) \times \text{conc. OH}';$$

hence:

$$\frac{K_a K_b x^2}{\gamma^2(1 - x)^2} = K_w,$$

or:

$$\frac{x}{\gamma(1 - x)} = \sqrt{\frac{K_w}{K_a.K_b}}$$

This is the well-known equation for the hydrolysis of such a salt; it signifies that when the salt is completely dissociated ($\gamma = 1$), the degree of hydrolysis is independent of the dilution. It has not, however, yet been pointed out, so far as I know, that the concentration of the hydrogen (and hydroxyl) ions in a solution of a weak salt must always be constant, whatever be the dilution, and whether the salt is completely dissociated or not. This follows at once from the above equations, for

$$\text{conc. H}^{\cdot} = \frac{K_a . x}{\gamma(1 - x)} = \sqrt{\frac{K_w . K_a}{K_b}} = \text{constant.}$$

A striking proof of this can be obtained colorimetrically. The addition of a few drops of the aniline acetate solution to a neutral solution of methyl-orange causes the same rise in colour as the addition of a large quantity. The results of actual experiments are shown below:

Aniline acetate.	Colour.	Mean.	conc. H˙.	x (For complete dissociation).
20	1·92	—	—	—
40	1·92	—	—	—
50	1·90	—	—	—
80	1·90	1·91	$0{\cdot}229 \times 10^{-4}$	0·560
100	1·90	—	—	—
200	1·91	—	—	—
500	1·90	—	—	—

The molecular colour is constant within the errors of observation when the concentration of aniline acetate varies from $N/20$ to $N/500$. From the colour, the concentration of the hydrogen ion is obtained as before, and then the degree of hydrolysis is calculated from the equation:

$$\frac{x}{1 - x} = \frac{\text{conc. H}^{\cdot}}{K_a},$$

K_a being $1{\cdot}8 \times 10^{-5}$.

In this way we find $x = 56{\cdot}0$ per cent. Arrhenius and Walker (*Zeitsch. physikal. Chem.*, 1889, **5**, 18) found that for the same salt the percentage hydrolysed was 55·5, as a mean of the values for six different dilutions ranging from $V = 12{\cdot}5$ to $V = 400$.

The two methods therefore give practically identical results.

From the hydrolysis of the chloride, we can calculate:

$$K_b = \frac{K_w}{0{\cdot}24 \times 10^{-4}} = \frac{1{\cdot}1}{0{\cdot}24} \times 10^{-10} \; (K_w = 1{\cdot}1 \times 10^{-14} \text{ at } 25^{\circ})$$
$$= 4{\cdot}6 \times 10^{-10}$$

from that of the acetate:

$$K_b = \frac{K_w . K_a}{(\text{conc. H}^{\cdot})^2} = \frac{1{\cdot}1 \times 10^{-14} \times 1{\cdot}8 \times 10^{-5}}{0{\cdot}0522 \times 10^{-8}}$$
$$= 3{\cdot}8 \times 10^{-10}.$$

This difference is within the error of hydrolysis measurement by any method. The colorimetric method used in the investigation seems to give too low values for the hydrolysis constant of the hydrochloride, so that K_b calculated from the hydrolysis of the acetate is probably more accurate. In any case the mean value:

$$K_b = 4{\cdot}2 \times 10^{-10} \text{ at } 25^{\circ}$$

cannot be far from the truth. The number accepted by Lundén ($4{\cdot}6 \times 10^{-10}$) appears therefore too high.

In conclusion, the results communicated in the present paper show that, with proper precautions, hydrolysis can be measured colorimetrically by means of methyl-orange, with an accuracy that compares favourably with that attained by other methods. The base should, however, have a dissociation constant less than 10^{-7}. For bases stronger than this, but weaker than ammonia, methyl-red will probably be found suitable. Since the apparatus and the method of working are extremely simple, there is no reason why the colorimetric method should not come into more extended use.

Summary.

It is shown that the degree of hydrolysis of aniline salts can be accurately determined by measuring the depth of colour of methyl-orange in the solution, and then calculating the concentration of hydrogen ions by means of the equations deduced in the preceding paper.

It is also pointed out that the concentration of hydrogen ions in a solution of a salt of a weak acid and a weak base is always the same, whatever the dilution and degree of dissociation of the salt.

The researches communicated in this and the preceding paper were carried out in the Davy-Faraday Laboratory of the Royal Institution. I should like to express here my thanks to the managers of the laboratory for the facilities they have placed at my disposal.

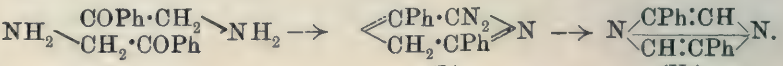
Davy-Faraday Laboratory,
Royal Institution.

CCLVII.—*Syntheses in the Epinephrine Series. Part II. The Formation and Properties of Some 2 : 5- and 2 : 6-Substituted Pyrazines and their Conversion into Amino-ketones and Imino-diketones.*

By Frank Tutin.

In a recent communication (Tutin, Caton, and Hann, Trans., 1909, **95**, 2113) it was shown that the action of ammonia on ω-chloro-*p*-hydroxyacetophenone did not result in the formation of ω-amino-*p*-hydroxyacetophenone, but yielded only resinous products. This result was considered somewhat remarkable, inasmuch as the analogous chloro-*mp*-dihydroxy-ketone readily yields the corresponding amine (D.R.-P. 155632). The behaviour of a number of ω-chloroacetophenone derivatives on heating with ammonia has therefore been investigated, with the result that it has been rendered evident that these compounds may be divided into three classes, according to the products which they yield on this treatment. Thus, ω-chloro-*mp*-dihydroxyacetophenone, on treatment with ammonia, behaves in a normal manner, yielding the corresponding amine. Only amorphous products result from the interaction of ammonia and ω-chloro-*p*-hydroxyacetophenone, *ω-chloro-*o*-methoxyacetophenone*, or *ω-chloro-*op*-dimethoxyacetophenone*. When, however, either ω-chloroacetophenone, ω-chloro-*p*-methoxyacetophenone, or *ω-chloro-*mp*-dimethoxyacetophenone* is heated with alcoholic ammonia, the principal product of the reaction is a mixture of 2:5- and 2:6-substituted pyrazines, in about equal proportions.

The formation of 2:5-diphenylpyrazine (II) from ω-bromoacetophenone and ammonia was studied by Gabriel (*Ber.*, 1908, **41**, 1127), who showed that, after replacement of the halogen, 3:6-dihydro-2:5-diphenylpyrazine (I) was formed, and that this then underwent spontaneous oxidation to the diphenylpyrazine, as follows:



$$NH_2\begin{matrix}COPh\cdot CH_2\\ CH_2\cdot COPh\end{matrix}NH_2 \rightarrow \begin{matrix}CPh\cdot CN_2\\ CH_2\cdot CPh\end{matrix}N \rightarrow N\begin{matrix}CPh:CH\\ CH:CPh\end{matrix}N.$$

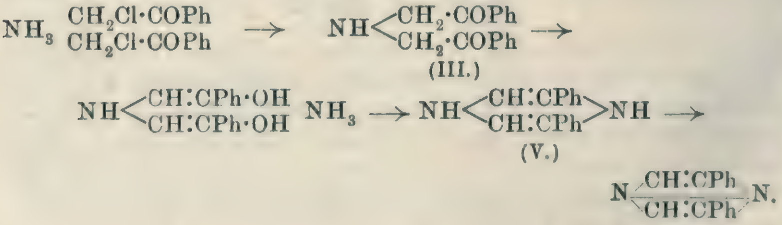
(I.) (II.)

The last-mentioned author, however, overlooked the fact that 2:6-diphenylpyrazine is also formed in this reaction, and the mode of production of this compound therefore remains to be explained. Gabriel (*loc. cit.*), however, identified diphenacylamine,

$$(Ph\cdot CO\cdot CH_2)_2NH,$$

as a product of the interaction of ω-bromoacetophenone and ammonia, and the present author has similarly obtained this base, as a minor product, from ω-chloroacetophenone.

It is now shown that diphenacylamine (III) and its derivatives are intermediate compounds in the formation of 2:6-substituted pyrazines, for they pass into the latter on heating with ammonia. The series of changes which results in the formation of 2:6-diphenylpyrazine (IV) from ω-chloroacetophenone and ammonia may therefore be represented as follows:



$$NH_3\begin{matrix}CH_2Cl\cdot COPh\\ CH_2Cl\cdot COPh\end{matrix} \rightarrow NH\begin{matrix}CH_2\cdot COPh\\ CH_2\cdot COPh\end{matrix} \rightarrow$$

(III.)

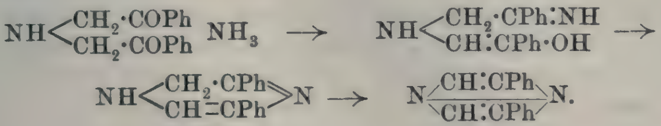
$$NH\begin{matrix}CH:CPh\cdot OH\\ CH:CPh\cdot OH\end{matrix}NH_3 \rightarrow NH\begin{matrix}CH:CPh\\ CH:CPh\end{matrix}NH \rightarrow$$

(V.)

$$N\begin{matrix}CH:CPh\\ CH:CPh\end{matrix}N.$$

(IV.)

According to this scheme the action of ammonia on diphenacylamine first results in the production of 1 : 4-*dihydro*-2 : 6-*diphenylpyrazine* (V), which then passes into 2 : 6-diphenylpyrazine by spontaneous oxidation. The change might, however, conceivably take place as follows:



$$NH{<}\begin{matrix}CH_2\cdot COPh\\ CH_2\cdot COPh\end{matrix}\ NH_3 \longrightarrow NH{<}\begin{matrix}CH_2\cdot CPh{:}NH\\ CH{:}CPh\cdot OH\end{matrix} \longrightarrow$$

$$NH{<}\begin{matrix}CH_2\cdot CPh\\ CH{=}CPh\end{matrix}{>}N \longrightarrow N{<}\begin{matrix}CH{:}CPh\\ CH{:}CPh\end{matrix}{>}N.$$

(VI.)

If this be the case, the intermediate compound will be 3 : 4-*dihydro*-2 : 6-*diphenylpyrazine* (VI).

The change which is here shown to occur on heating compounds of the type $(R\cdot CO\cdot CH_2)_2NH$ with ammonia does not appear to have been observed before, and it therefore seems to afford a new, general method for the production of 2 : 6-substituted pyrazines.

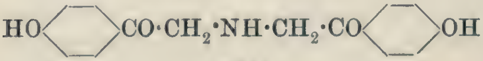
The interaction of ammonia and ω-chloro-*p*-methoxyacetophenone proceeds similarly to that of ω-chloroacetophenone and ammonia, yielding, as principal products, pp′-*dimethoxy*-2 : 5-*diphenylpyrazine* (m. p. 223°) and pp′-*dimethoxy*-2 : 6-*diphenylpyrazine* (m. p. 137·5°). The former of these two compounds is of particular interest, as, on fusion, it passes into the "liquid-crystalline" state, and this phase persists over an exceptionally large range of temperature, namely, 41·4°. *pp*′-Dimethoxy-2 : 5-diphenylpyrazine therefore represents a new addition to the already considerable list of "liquid-crystalline" *p*-anisyl derivatives, but it appears to be the first compound of this class in which the anisyl group is attached to a ring. A further interesting property of *pp*′-dimethoxy-2 : 5-diphenylpyrazine is that its solutions exhibit a violet-blue fluorescence, a behaviour which has not previously been observed amongst pyrazine derivatives. Furthermore, on the addition of a drop of concentrated hydrochloric or sulphuric acid to a chloroform solution of this base, a most brilliant green fluorescence is produced. *pp*′-Dimethoxy-2 : 6-diphenylpyrazine behaves in marked contrast to its 2 : 5-substituted isomeride, as it fluoresces but slightly, and only in neutral solution, and it does not pass into the "liquid-crystalline" state.

ω-*Chloro*-mp-*dimethoxyacetophenone* yielded mm′pp′-*tetramethoxy*-2 : 5-*diphenylpyrazine* (m. p. 208°) and mm′pp′-*tetramethoxy*-2 : 6-*diphenylpyrazine* (m. p. 160°) on treatment with ammonia, neither of which passes into the "liquid-crystalline" state. The former compound is, however, strongly fluorescent, but only in neutral solution.

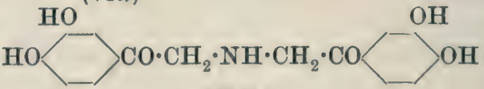
It is furthermore shown in the present communication that the series of changes which result respectively in the formation of

2:5-substituted pyrazines from ω-aminoacetophenone or its derivatives, and in the conversion of diphenacylamine or its derivatives into 2:6-substituted pyrazines, may be reversed by means of hydriodic acid. Thus, when 2:5-diphenylpyrazine is heated with hydriodic acid, reduction followed by hydrolysis occurs, resulting in the formation of two molecules of ω-aminoacetophenone hydriodide. Similarly, 2:6-diphenylpyrazine, when analogously treated, is converted into *diphenacylamine hydriodide* and ammonium iodide. Of course, when employing the pyrazine derivatives containing methoxyl groups, the methyl group is also eliminated by the hydriodic acid. This reaction therefore has afforded a new method of preparing ω-amino-*p*-hydroxyacetophenone and ω-amino-*mp*-dihydroxyacetophenone, two bases which are of interest on account of their physiological activity. The former of these bases was previously prepared by the present author in conjunction with Messrs. Caton and Hann (*loc. cit.*) from ω-chloro-*p*-acetoxyacetophenone, whilst the latter base is of special importance on account of its near relationship to epinephrine.

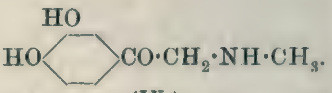
pp′-*Dihydroxydiphenacylamine* and mm′pp′-*tetrahydroxydiphenacylamine* have been prepared by the action of hydriodic acid on the previously-mentioned methoxy-2:6-diphenylpyrazines. It will readily be seen from a comparison of the formulæ given below that *pp′*-dihydroxydiphenacylamine (VII) and, especially, *mm′pp′*-tetrahydroxydiphenacylamine (VIII) are closely related to the ketone derived from epinephrine (IX), as also to the above-mentioned two ω-aminohydroxyacetophenones:



(VII.)



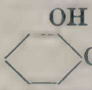
(VIII.)



(IX.)

It was therefore to be expected that these two diphenacylamine derivatives would be possessed of physiological activity, and their properties have accordingly been investigated in the Wellcome Physiological Research Laboratories by Dr. H. H. Dale, to whom the author is indebted for the following and the subsequently mentioned physiological experiments. It was found that each of these compounds, in the form of salts, when injected intravenously into cats, caused a rise in blood-pressure, *pp′*-dihydroxydiphenacylamine (VII) having an action similar to that of the related compound, ω-amino-*p*-hydroxyacetophenone (Tutin, Caton, and Hann, *loc. cit.*), whilst the corresponding tetrahydroxy-base (VIII) had a greater activity, more resembling that of the ketone derived from epinephrine (IX).

It has already been mentioned that ω-chloro-*o*-methoxyacetophenone and ω-chloro-*op*-dimethoxyacetophenone yield only amorphous products when heated with ammonia, whereas the analogous compounds containing the methoxyl groups in the *m*- and *p*-positions readily yield substituted pyrazines. It therefore appears that the presence of a methoxyl group in the *o*-position with respect to the side-chain precludes the formation of pyrazines from ω-chloroacetophenone derivatives, although the reason for this is not apparent.

On account of the above-mentioned property of the *o*-substituted ω-chloroacetophenone derivatives here described, it was impossible to obtain from them the corresponding ω-aminohydroxyacetophenones in the way which has already been noted in connexion with the preparation of ω-amino-*p*-hydroxyacetophenone from ω-chloro-*p*-methoxyacetophenone. Recourse was therefore had to the use of potassium phthalimide, and by this means derivatives and salts of *ω-amino-o-hydroxyacetophenone* and *ω-amino-*op*-dihydroxyacetophenone* have been obtained. When examined physiologically, the *hydriodide* of the *o*-hydroxy-base was found to be practically inactive, whilst the corresponding salt of the *op*-dihydroxy-base had no greater activity than the analogous *p*-hydroxy-compound. It is therefore seen that hydroxyl groups in the *o*-position with respect to the side-chain are devoid of physiological activity in the class of compounds under consideration, a result which is in harmony with a previous observation of Dr. Dale, who found *o*-hydroxy-β-phenylethylamine,  $CH_2 \cdot CH_2 \cdot NH_2$, to be inert, whilst the analogous *p*-compound is strongly active (Barger, Trans., 1909, **95**, 1123).

ω-Chloro-*o*-methoxyacetophenone is formed, together with the corresponding *p*-compound, by the action of aluminium chloride on chloroacetyl chloride and anisole. The further action of aluminium chloride on ω-chloro-*o*-methoxyacetophenone results in the formation of *ω-chloro-o-hydroxyacetophenone*. The latter substance differs from the corresponding *p*-compound, inasmuch as it is quite insoluble in aqueous sodium carbonate, thus showing how the relative positions of the groups in the benzene nucleus affect the acidity of the hydroxyl group.

The above-mentioned substituted ω-aminoacetophenones, containing a hydroxyl group in the *o*-position with respect to the side-chain, differ markedly in their properties from the previously-mentioned analogous compounds which are substituted in the *m*- or *p*-position, inasmuch as they condense and oxidise, when dissolved in neutral solvents, to form 2 : 5-substituted pyrazines. oo′-*Dihydroxy*-2 : 5-*diphenylpyrazine* and oo′pp′-*tetrahydroxy*-2 : 5-*diphenylpyrazine* have thus been prepared.

The two *o*-substituted ω-aminoacetophenones described also show a singular behaviour when benzoylated, either by the Schotten-Baumann method or in pyridine solution, for, when thus treated, they yield benzoyl derivatives of internal anhydrides. It would appear possible that these condensation products are 1-*benzoylindoxyl* and 6-*benzoyloxy*-1-*benzoylindoxyl* respectively.

Gabriel (*loc. cit.*), from his work on ω-aminoacetophenone, concluded that α-amino-ketones of this type were incapable of existence in the free state, but always underwent condensation when liberated from their salts. It is evident, however, from the results given in the present paper that this is not invariably the case. Thus, ω-aminoacetophenone, ω-amino-*p*-methoxyacetophenone, ω-amino-*mp*-dimethoxyacetophenone, and ω-amino-*o*-hydroxyacetophenone condense spontaneously, yielding pyrazine derivatives in the manner shown by Gabriel. ω-Amino-*p*-hydroxyacetophenone and ω-amino-*mp*-dihydroxyacetophenone, on the other hand, cannot be caused to condense; whilst ω-amino-*op*-dihydroxyacetophenone possesses properties between those of these two groups, for it can be obtained in the free state, although it condenses somewhat readily.

EXPERIMENTAL.

Interaction of ω-Chloroacetophenone and Ammonia.

Chloroacetyl chloride was dissolved in an excess of benzene, and one molecular proportion of aluminium chloride added. A violent reaction ensued, and, when this had subsided, ice and hydrochloric acid were added. The aqueous layer was then separated, and, after washing the benzene solution with water, the greater part of the solvent was removed from it. On adding light petroleum to the concentrated liquid thus obtained, ω-chloroacetophenone separated in glistening plates, melting at 59°. The yield was nearly quantitative.

Fifteen grams of ω-chloroacetophenone were heated for one and a-half hours at 100° in sealed tubes with an excess of alcoholic ammonia. After allowing the contents of the tubes to cool, the solid which had separated was collected, washed with alcohol, and then extracted repeatedly with boiling xylene. The material undissolved by this treatment consisted entirely of ammonium chloride, but on concentrating the xylene extracts, a compound separated in plates, melting at 194°. As thus obtained, this substance possessed a dark bluish-green colour, and was only obtained colourless after being treated, in acetic acid solution, with a small amount of potassium permanganate dissolved in the same solvent. When crystallised from xylene after this treatment, it formed large, colourless plates, melting at 194°, and was identified as 2:5-diphenylpyrazine (Found, C = 79·5; H = 5·1. Calc., C = 79·3; H = 5·0 per cent.)

This compound was first prepared by Staedel and Rügheimer (*Ber.*, 1876, **9**, 563), who described it under the name of "*iso*indol." As subsequently obtained by Staedel and Kleinschmidt (*ibid.*, 1880, **13**, 836), it was observed to exhibit diverse colours, and they regarded it as being "idiochromatic." Pure 2:5-diphenylpyrazine is, however, quite colourless, as has been shown by Gabriel (*Ber.*, 1908, **41**, 1127), who prepared it by the interaction of ω-bromoacetophenone and ammonia.

The original alcoholic filtrate from the 2:5-diphenylpyrazine and ammonium chloride was evaporated to a low bulk and largely diluted with benzene. The filtered liquid was then again evaporated as far as possible, and the residue dissolved in alcoholic hydrogen chloride, when the mixture rapidly became dark brown, but no blue colour was developed (see below). The solution was concentrated somewhat, and hot ethyl acetate added, when, on cooling the mixture, a crystalline substance separated in needles, which were collected and washed with a mixture of ethyl acetate and alcoholic hydrogen chloride. The product so obtained was dissolved in the minimum amount of absolute alcohol, and a little alcoholic hydrogen chloride added, when it immediately separated in soft, almost colourless needles, melting at about 189°:

0·2020 gave 0·1060 AgCl. Cl = 13·0.

$C_{16}H_{12}N_2,HCl$ requires Cl = 13·2 per cent.

This substance was identified as 2:6-*diphenylpyrazine monohydrochloride*,* since it yielded 2:6-diphenylpyrazine, which formed colourless needles, melting at 90°. (Found, C = 79·3; H = 5·2. Calc., C = 79·3; H = 5·0 per cent.)

2:6-Diphenylpyrazine monohydrochloride is almost insoluble in benzene or ethyl acetate, but it dissolves fairly readily in alcohol, owing to the fact that it becomes, for the most part, dissociated. It is not stable in moist air, and is instantly dissociated when brought in contact with water.

Gabriel (*loc. cit.*) did not note the formation of 2:6-diphenylpyrazine when he investigated the interaction of ω-bromoacetophenone and ammonia, but it would appear certain that it must have been present in the reaction mixture examined by him.

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* It has been found that the pyrazines are diacidic bases, and yield two series of salts (compare following paper).

The original filtrate from the 2: 6-diphenylpyrazine hydrochloride was dark brown, and contained considerable resinous matter. It was largely diluted with water, filtered from the precipitated resin, concentrated somewhat, and treated with animal charcoal. On allowing the clear liquid to cool, a somewhat sparingly soluble compound separated, which melted at about 235°, and was subsequently identified as diphenacylamine hydrochloride, a compound which has been described by Gabriel (*loc. cit.*).

In a subsequent preparation of the above-described 2: 5- and 2: 6-diphenylpyrazines, a quantity (40 grams) of ω-chloroacetophenone was heated in an autoclave with an excess of alcoholic ammonia, the mixture being subsequently kept for fourteen days before it was worked up. After separating the ammonium chloride and 2: 5-diphenylpyrazine in the manner already described, the residual solution containing the 2: 6-base, which was of a much more pronounced red colour, and appeared to be freer from resinous matter than that obtained in the previous preparation, was mixed with a large volume of ether and extracted several times with a mixture of concentrated hydrochloric acid (1 part) and water (2 parts). This caused the separation of some brown, resinous matter, which was removed. The ethereal liquid was then evaporated, and the red residue dissolved in absolute alcohol, and a solution of hydrogen chloride in the same solvent added. The liquid then became deep blue, and, on cooling the mixture after adding some ethyl acetate, a solid separated, which, when collected, was seen to consist of a mixture of white and deep blue needles, the former predominating. The separation of these two products was tedious, but was eventually effected by taking advantage of the fact that the blue *hydrochloride* was somewhat more sparingly soluble in a boiling solution of hydrogen chloride in absolute alcohol than was the white one, which consisted of 2: 6-diphenylpyrazine hydrochloride. The blue compound crystallised in small needles, which had no definite melting point, and were only stable in dry air or in an anhydrous solvent in the presence of a moderate excess of hydrogen chloride. The amount obtained was only about 0·5 gram, and consequently the formula could not be established:

0·3506 gave 0·4791 AgCl. Cl = 33·8 per cent.

The *base* obtained from this deep blue hydrochloride crystallised from alcohol in small tufts of brilliant scarlet crystals, melting at 195°. It was readily soluble in chloroform, ethyl acetate, or benzene, but only moderately so in alcohol. On exposing a solution of this scarlet-coloured base in chloroform or benzene to direct sunlight, the colour was discharged in half-an-hour, a compound crystallising in yellow needles being formed.

Preparation of ω-Chloro-o- and -p-*methoxyacetophenones.*

ω-Chloro-*p*-methoxyacetophenone was prepared by Kunckell and Johannssen (*Ber.*, 1897, **30**, 1715; 1898, **31**, 170) by the interaction of anisole and chloroacetyl chloride in the presence of aluminium chloride. Mr. F. W. Caton, who conducted this operation for the present author, found it important to avoid the use of any excess of aluminium chloride and not to employ heat, as the methyl group is very easily eliminated. With the object of avoiding this hydrolysis, experiments were made with the use of sublimed ferric chloride, but the yield of condensed product so obtained was only small.

One molecular proportion of anisole was mixed with rather more than an equivalent amount of chloroacetyl chloride, and, after diluting the mixture with three times its volume of carbon disulphide, one molecular proportion of powdered aluminium chloride was cautiously added, the flask being kept cool during this operation. After three hours the carbon disulphide was decanted, the residue being decomposed with ice and hydrochloric acid and the product extracted with ether. The ethereal liquid was then shaken with aqueous sodium hydroxide, which removed small amounts of hydrolysed product and red resin, after which the solvent was evaporated. On fractionally crystallising the residue from alcohol, it was found to consist, for the most part, of ω-chloro-*p*-methoxyacetophenone (m. p. 102°), which formed long needles, but the more soluble fraction contained a second substance. This compound formed large, colourless, diamond-shaped plates, which, after being separated mechanically from the greater part of the *p*-compound and submitted to several recrystallisations, melted at 69°:

0·2154 gave 0·4571 CO_2 and 0·0993 H_2O. C = 57·9; H = 5·1.
0·2288 „ 0·1778 AgCl. Cl = 19·2.

$C_9H_9O_2Cl$ requires C = 58·5; H = 4·9; Cl = 19·2 per cent.

This substance was evidently *ω-chloro-*o*-methoxyacetophenone*, since it readily yielded salicylic acid on fusion with potassium hydroxide.

This appears to be the first time that the formation of an *o*-monosubstituted ketone by means of the Friedel and Crafts' reaction has been noted, although phenyl *o*-tolyl ketone has been stated to be formed by the interaction of toluene and benzoic acid in the presence of phosphoric oxide (Kollarits and Merz, *Ber.*, 1873, **6**, 538).

ω-Chloro-*o*-methoxyacetophenone is slightly volatile at the ordinary temperature, and sublimes readily on heating. It is more volatile in steam than is the corresponding *p*-compound, and may be approximately separated from the latter by taking advantage of this property. When brought into contact with the skin, it causes considerable smarting, and it has an extremely irritant action on the eyes.

Attempts to prepare *o*-methoxydiphenylpyrazines by heating ω-chloro-*o*-methoxyacetophenone with alcoholic ammonia in sealed tubes resulted only in the formation of resinous products.

*ω-Chloro-*o*-hydroxyacetophenone.*

ω-Chloro-*o*-methoxyacetophenone was dissolved in carbon disulphide, one molecular proportion of powdered aluminium chloride added, and the mixture heated for two hours under a reflux condenser. The solvent was then removed, and the residue heated at 100° for ten minutes, after which ice and hydrochloric acid were added, and the product extracted with ether. On shaking the ethereal liquid with a solution of sodium carbonate, nothing was removed, but subsequent treatment with aqueous sodium hydroxide extracted a relatively small proportion of oily matter. The ethereal liquid, on evaporation, yielded a considerable quantity of unchanged ω-chloro-*o*-methoxyacetophenone, this compound being evidently much more stable towards aluminium chloride than is the corresponding *p*-derivative. The oil which had been removed by sodium hydroxide was dissolved in ether, and light petroleum added, which caused the separation of a viscid, red product, whereupon the mixture was shaken with animal charcoal, and filtered. After concentrating the filtrate, a substance separated in yellow, flattened needles, which, after recrystallisation from alcohol, melted at 101°:

0·1238 gave 0·2546 CO_2 and 0·0490 H_2O. $C = 56{\cdot}0$; $H = 4{\cdot}4$.

$C_8H_7O_2Cl$ requires $C = 56{\cdot}3$; $H = 4{\cdot}3$ per cent.

This substance was therefore *ω-chloro-*o*-hydroxyacetophenone*, $HO{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Cl$. It differed from the corresponding *p*-compound in being insoluble in aqueous sodium carbonate (compare Tutin, Caton, and Hann, Trans., 1909, **95**, 2118).

*Interaction of ω-Chloro-*p*-methoxyacetophenone and Ammonia.*

ω-Chloro-*p*-methoxyacetophenone was heated in an autoclave for three hours at 110° with a large excess of alcoholic ammonia. When cool, the solid contained in the dark-coloured reaction mixture was collected and washed, first with alcohol, and subsequently with water. The residue was crystallised from xylene, when it separated in large leaflets, melting at 222°. The substance, as thus obtained, could not be rendered colourless by recrystallisation, but different preparations of it exhibited diverse tints, such as dull green, purplish, or greenish-yellow. It was, however, rendered colourless by the means previously found useful in the case of 2 : 5-diphenylpyrazine (p. 2501), but the melting point was practically unchanged by this treatment. On crystallising the purified substance from glacial acetic acid or xylene, it formed large, colourless leaflets, but when crystallised from chloroform or ethyl acetate it separated in hexagonal plates:

0·1088 gave 0·2947 CO_2 and 0·0556 H_2O. C = 73·9; H = 5·7.
0·3246 ,, 29·0 c.c. N_2 (moist) at 20° and 728 mm. N = 9·8.
$C_{18}H_{16}O_2N_2$ requires C = 73·9; H = 5·5; N = 9·6 per cent.

A molecular-weight determination by the cryoscopic method gave the following result:

0·3153, in 33·2 of phenol, gave $\Delta t = -0·30°$. M.W. = 243.
$C_{18}H_{16}O_2N_2$ requires M.W. = 292.

Several attempts were made to estimate the number of methoxyl groups in this substance by Perkin's modification of Zeisel's method, but accurate results could not at first be obtained, owing to the great stability of the compound. It was eventually ascertained, however, that the methyl groups are rapidly eliminated if some glacial acetic acid be added to the hydriodic acid employed:

0·2096 gave 0·3366 AgI. OMe = 21·1.
$C_{16}H_{10}N_2(OMe)_2$ requires OMe = 21·2 per cent.

The compound was evidently pp′-*dimethoxy*-2 : 5-*diphenylpyrazine*, $C_4H_2N_2(C_6H_4\cdot OMe)_2$, and its constitution was subsequently confirmed by its conversion by hydriodic acid into *ω-amino*-p-*hydroxyacetophenone hydriodide* and methyl iodide (p. 2520).

On heating *pp′*-dimethoxy-2 : 5-diphenylpyrazine, fusion occurs at 223°, and the substance passes into a "liquid-crystalline" state. This phase persists until a temperature of 265·4° is reached, when the "crystalline" liquid phase instantly passes into the normal liquid state. At the point of change it can easily be observed that the two liquid phases are immiscible, and the "liquid-crystalline" product appears to possess the greater density. The reverse change, from the normal liquid to the "liquid-crystalline" phase, occurs at precisely the same temperature, and is exhibited in a striking manner when viewed through crossed Nicol's prisms. The point of change from the "liquid-crystalline" to the normal liquid phase, and vice versa, of *pp′*-dimethoxy-2 : 5-diphenylpyrazine is a much more delicate criterion of the purity of this substance than is its melting point, as a mere trace of impurity causes a very appreciable lowering of the temperature of transition from one liquid phase to the other, whilst an amount of extraneous substance sufficient to cause a depression of the melting point by about 3° completely extinguishes the "liquid-crystalline" phase.

pp′-Dimethoxy-2 : 5-diphenylpyrazine is practically insoluble in ether or alcohol, very sparingly soluble in chloroform, benzene, or ethyl acetate, moderately soluble in boiling xylene, and more readily so in glacial acetic acid. Its dilute solution in chloroform exhibits a violet-blue fluorescence, and when a drop of concentrated hydrochloric acid is added, a yellow colour is produced, accompanied by a most brilliant green fluorescence.

The original, dark-coloured, alcoholic filtrate from the ammonium chloride and *pp′*-dimethoxy-2 : 5-diphenylpyrazine was evaporated to dryness, the residue extracted with benzene, the solution evaporated, and the residue dissolved in absolute alcohol. A solution of hydrogen chloride in absolute alcohol was then added, when, after concentrating the solution, it was mixed with hot ethyl acetate. On cooling the mixture, a compound separated in yellow needles, which were collected, washed with a mixture of alcoholic hydrogen chloride and ethyl acetate, and recrystallised by dissolving them in absolute alcohol, adding alcoholic hydrogen chloride, concentrating the mixture, and then diluting it with ethyl acetate. Soft, yellow needles were thus obtained, which melted at about 178—180°:

0·2420 gave 0·1003 AgCl. Cl = 10·3.
$C_{18}H_{16}O_2N_2$,HCl requires Cl = 10·8 per cent.

This salt proved to be pp′-*dimethoxy*-2 : 6-*diphenylpyrazine monohydrochloride*, $C_4H_2N_2(C_6H_4{\cdot}OMe)_2$,HCl. It dissolves sparingly in ethyl acetate or chloroform containing an excess of hydrogen chloride, but is unstable in moist air, and is dissociated by alcohol or water.

pp′-*Dimethoxy*-2 : 6-*diphenylpyrazine*, $C_4H_2N_2(C_6H_4{\cdot}OMe)_2$, obtained from the above-described salt by treatment with water or alcohol, crystallised from the latter solvent in colourless needles, melting at 137·5°:

0·0987 gave 0·2670 CO_2 and 0·0505 H_2O. C = 73·8; H = 5·7.
$C_{18}H_{16}O_2N_2$ requires C = 73·9; H = 5·5 per cent.

pp′-Dimethoxy-2 : 6-diphenylpyrazine is very readily soluble in chloroform, ethyl acetate, benzene, or xylene, but only moderately so in alcohol. Its neutral solutions exhibit a slight blue fluorescence, but this is destroyed by the addition of concentrated hydrochloric acid. It does not pass into a "liquid-crystalline" state on fusion. The constitution of *pp′*-dimethoxy-2 : 6-diphenylpyrazine was subsequently proved by its conversion by means of hydriodic acid into methyl iodide, ammonium iodide, and pp′-*dihydroxydiphenacylamine hydriodide* (p. 2522).

The filtrate from the crude *pp′*-dimethoxy-2 : 6-diphenylpyrazine hydrochloride was dark brown, and contained considerable resinous matter. It was digested with aqueous hydrochloric acid, filtered, and the filtrate treated with animal charcoal. After concentrating the liquid thus obtained, it deposited a relatively small amount of a sparingly soluble hydrochloride. This was recrystallised from water, when it formed leaflets, melting at 256°:

0·2459 gave 0·1003 AgCl. Cl = 10·0.

$C_{18}H_{19}O_4N,HCl$ requires Cl = 10·1 per cent.

This salt was doubtless pp′-*dimethoxydiphenacylamine hydrochloride*, $(MeO\cdot C_6H_4\cdot CO\cdot CH_2)_2NH,HCl$, as it was obtained in a manner analogous to that which resulted in the formation of diphenacylamine hydrochloride from ω-chloroacetophenone, and its properties are strictly analogous to those of the latter salt. Moreover, from evidence given in the latter part of this communication, it is evident that *pp′*-dimethoxydiphenacylamine must have been formed during the interaction of ammonia and ω-chloro-*p*-methoxyacetophenone, since the former base is an intermediate compound in the production of the above-described *pp′*-dimethoxy-2 : 6-diphenylpyrazine.

It has already been shown in connexion with the preparation of the 2 : 5- and 2 : 6-diphenylpyrazines that if the reaction mixture were kept for some time before it was worked up, a highly-coloured by-product was formed, together with these bases. This is also the case when working with the *p*-methoxy-derivatives, but in the latter instance several other compounds were also obtained in small amounts, possibly owing to the fact that the reaction mixture was examined much more fully than in the former case.

ω-Chloro-*p*-methoxyacetophenone was heated with alcoholic ammonia as above described, but the reaction mixture was kept for three weeks before being examined. The *pp′*-dimethoxy-2 : 5-diphenylpyrazine was isolated as before described, but with the use of chloroform instead of xylene. The mother liquors then yielded a small amount of a compound, which formed soft, colourless needles, melting at 232—233°. On working up the original filtrate from the *pp′*-dimethoxy-2 : 5-diphenylpyrazine and ammonium chloride in the manner previously described, a mixture of *pp′*-dimethoxy-2 : 6-diphenylpyrazine and another salt was obtained. The latter compound was evidently the *p*-methoxy-derivative of the blue hydrochloride previously described; it was dark green, and was separated from the salt of the pyrazine derivative in a manner analogous to that employed in connexion with the previously-described blue compound. The mother liquors from these hydrochlorides yielded, together with traces of other compounds, a substance which formed yellow leaflets, melting at 213—214°, but did not fluoresce when treated in chloroform solution with hydrochloric acid. The deep green-coloured hydrochloride melted quite indefinitely, owing to dissociation, and this change was also readily brought about by treatment with any solvent which did not contain an excess of anhydrous hydrogen chloride. It yielded a deep crimson-coloured base, crystallising from alcohol in small, lustrous prisms, which were so dark red as to appear almost black, and melted at about 165°. This compound, like the corresponding phenyl derivative previously described, is decolorised by exposure to direct sunlight when dissolved, yielding a yellow substance, which formed needles (m. p. about 255°) from xylene. The amounts of these various by-products obtained was small, and their investigation was not further pursued.

*Derivatives of ω-Amino-*p*-methoxyacetophenone.*

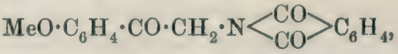
It would appear that the above-described *pp′*-dimethoxy-2:5-diphenylpyrazine must have been formed by the condensation of two molecules of *ω-amino-*p*-methoxyacetophenone*, followed by spontaneous oxidation of the resulting pp′*-dimethoxy-*3:6*-dihydro-*2:5*-diphenylpyrazine* in a manner analogous to that which has been shown by Gabriel (*loc. cit.*) to result in the formation of 2:5-diphenylpyrazine from ω-aminoacetophenone. With the object, therefore, of verifying this conclusion, ω-amino-*p*-methoxyacetophenone was prepared, in the form of its hydrochloride, as follows.

ω-Chloro-*p*-methoxyacetophenone was heated for some time in a nickel crucible with rather more than one molecular proportion of potassium phthalimide. The reaction mixture was then extracted with boiling xylene, and the product which crystallised from this solvent after concentration was repeatedly boiled with large quantities of water for the removal of unchanged phthalimide. On recrystallising the residue from xylene, glistening leaflets, melting at 164—165°, were obtained:

0·1437 gave 0·3650 CO_2 and 0·0604 H_2O. C = 69·2; H = 4·6.

$C_{17}H_{13}O_4N$ requires C = 69·2; H = 4·4 per cent.

*ω-Phthalimino-*p*-methoxyacetophenone,*



$$\mathrm{MeO{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}N}{<}\begin{smallmatrix}\mathrm{CO}\\ \mathrm{CO}\end{smallmatrix}{>}\mathrm{C_6H_4},$$

is very sparingly soluble in alcohol, ethyl acetate, or chloroform, but dissolves more readily in glacial acetic acid or boiling xylene.

The above-described phthalide derivative was boiled for eight hours with concentrated hydrochloric acid, when it gradually passed into solution. The mixture was then deprived of phthalic acid by means of ether, and evaporated to dryness under diminished pressure. On crystallising the residue from alcohol, *ω-amino*-p-*methoxyacetophenone hydrochloride*,

$$MeO\cdot C_6H_4\cdot CO\cdot CH_2\cdot NH_2,HCl,$$

was obtained in small, colourless prisms, which melted and decomposed at 204°, after having become red:

0·2121 gave 0·1408 AgCl. Cl=16·4.

$C_9H_{11}O_2N,HCl$ requires Cl=16·6 per cent.

When an alkali is added to an aqueous solution of ω-amino-*p*-methoxyacetophenone hydrochloride, no immediate separation of base occurs. The mixture, however, rapidly darkens somewhat, and, after some time, a dark-coloured, semi-crystalline product separates. On purification, this yielded *pp′*-dimethoxy-2 : 5-diphenylpyrazine (m. p. 223°), thus proving that a change analogous to that observed by Gabriel (*loc. cit.*) had occurred.

ω-Amino-p-*methoxyacetophenone Platinichloride*,

$$(MeO\cdot C_6H_4\cdot CO\cdot CH_2\cdot NH_2)_2H_2PtCl_6.$$

—This derivative crystallised very readily in deep yellow leaflets, and melted and decomposed at 225—228°:

0·1434 gave 0·0373 Pt. Pt=26·0.

$(C_9H_{11}O_2N)_2H_2PtCl_6$ requires Pt=26·3 per cent.

ω-Amino-p-*methoxyacetophenone Aurichloride*,

$$MeO\cdot C_6H_4\cdot CO\cdot CH_2\cdot NH_2,HAuCl_4.$$

—The *aurichloride* did not crystallise readily, but was eventually obtained in handsome, golden-coloured leaflets, which melted at 74°, and evidently contained water of crystallisation:

0·2024 gave 0·0762 Au. Au=37·6.

$C_9H_{11}O_2N,HAuCl_4,H_2O$ requires Au=37·6 per cent.

ω-Amino-p-*methoxyacetophenone picrate*, $C_9H_{11}O_2N,C_6H_3O_7N_3$, formed small, bright yellow leaflets, which, like the preceding compound, contained water of crystallisation. It melted and decomposed at 185°.

The *mercurichloride* crystallised very readily in long, colourless needles, which melted at 171°.

ω-Chloro-mp-*dimethoxyacetophenone*.

Catechol was methylated by means of methyl sulphate,* and the resulting veratrole purified by distillation. The veratrole was then dissolved in carbon disulphide, an equivalent amount of chloroacetyl chloride added, and then one molecular proportion of powdered aluminium chloride introduced. The mixture was heated on a water-bath for two hours, but the reaction which ensued was by no means violent. The carbon disulphide was then removed and the residue decomposed by ice and hydrochloric acid, the product being extracted with ether. On shaking the ethereal liquid with aqueous potassium hydroxide, a small quantity of demethylated product was removed. The ether was then evaporated, and the residue deprived of a fairly large proportion of unchanged veratrole by means of steam. The non-volatile product was crystallised from alcohol, when it yielded *ω-chloro*-mp-*dimethoxyacetophenone*, $(MeO)_2C_6H_3{\cdot}CO{\cdot}CH_2{\cdot}Cl$, which formed small, colourless prisms, melting at 101°:

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* Perkin and Weizmann (Trans., 1906, **89**, 1649) state that an almost quantitative yield of veratrole may be obtained by treating 100 grams of catechol with 75 grams of methyl sulphate and 150 grams of potassium hydroxide. The figures

0·1172 gave 0·2394 CO_2 and 0·0538 H_2O. C = 55·8; H = 5·1.

$C_{10}H_{11}O_3Cl$ requires C = 55·9; H = 5·1 per cent.

ω-Chloro-*mp*-dimethoxyacetophenone is moderately soluble in alcohol, but much more readily so in ethyl acetate or chloroform. When in the dry state, it occasions violent sneezing.

The Interaction of ω-Chloro-mp-*dimethoxyacetophenone and Ammonia.*

ω-Chloro-*mp*-dimethoxyacetophenone was heated in an autoclave for three hours at 110° with a large excess of absolute alcoholic ammonia. When cool, the solid contained in the reaction mixture was collected, washed with alcohol, and then extracted many times with boiling xylene. The xylene extracts, on cooling, deposited a dark red, crystalline powder, melting at 208°. After treatment with a small amount of potassium permanganate in glacial acetic acid solution, in the manner previously described, it separated from glacial acetic acid in light grey needles, which melted at the same temperature as before this treatment:

0·1130 gave 0·2834 CO_2 and 0·0590 H_2O. C = 68·4; H = 5·8.

$C_{20}H_{20}O_4N_2$ requires C = 68·2; H = 5·7 per cent.

This compound was evidently mm′pp′-*tetramethoxy*-2 : 5-*diphenylpyrazine*, $C_6H_4(OMe)_2{\cdot}C_4H_2N_2{\cdot}C_6H_3(OMe)_2$, and its constitution was subsequently confirmed by its conversion into *ω-amino*-mp-*dihydroxyacetophenone hydriodide* and methyl iodide by the action of hydriodic acid (p. 2520). It is insoluble, or nearly so, in all the usual solvents with the exception of glacial acetic acid and boiling xylene, and in the latter solvent it dissolves but sparingly. Its much greater

given are, however, obviously incorrect, since the amount of catechol mentioned would require theoretically 229 grams of methyl sulphate and 102 grams of the alkali.

solubility in glacial acetic acid than in any other liquid employed appeared to be due to salt formation, as the solution was orange-yellow, and it was subsequently found that the tetramethoxydiphenylpyrazines are more strongly basic than the other compounds of this class described in the present communication. A very dilute solution of *mm′pp′*-tetramethoxy-2 : 5-diphenylpyrazine in chloroform exhibits a strong blue fluorescence, but this phenomenon disappears on the addition of a drop of concentrated hydrochloric acid, a non-fluorescent, deep yellow liquid being produced. On fusion, this pyrazine derivative does not pass into a "liquid-crystalline" state, as is the case with the corresponding *pp′*-dimethoxy-compound.

The original alcoholic filtrate from the *mm′pp′*-tetramethoxy-2 : 5-diphenylpyrazine and ammonium chloride was evaporated to dryness, the residue extracted with benzene, the solution again evaporated, and the product so obtained dissolved in a small amount of absolute alcohol and a solution of hydrogen chloride in the same solvent added. On cooling the dark brown mixture, a compound separated in deep yellow needles. This was collected, washed with alcoholic hydrogen chloride, and recrystallised from absolute alcohol by the addition of a solution of hydrogen chloride in this solvent, when long, deep yellow, soft needles were obtained, which melted at about 195—200°:

0·2030 gave 0·0730 AgCl. Cl = 8·9.

$C_{20}H_{20}O_4N_2,HCl$ requires Cl = 9·1 per cent.

This compound was mm′pp′-*tetramethoxy*-2 : 6-*diphenylpyrazine monohydrochloride*, $C_6H_3(OMe)_2\cdot C_4H_2N_2\cdot C_6H_3(OMe)_2,HCl$. It was readily dissociated by water, or by alcohol, unless the latter contained an excess of hydrogen chloride. It yielded mm′pp′-*tetramethoxy*-2 : 6-*diphenylpyrazine*, which, when crystallised from alcohol, formed long, almost colourless needles, melting at 160°:

0·1079 gave 0·2734 CO_2 and 0·0563 H_2O. C = 68·0; H = 5·8.

$C_{20}H_{20}O_4N_2$ requires C = 68·2; H = 5·7 per cent.

This base was rather sparingly soluble in alcohol, but readily so in benzene, xylene, chloroform, glacial acetic acid, or ethyl acetate, and differed from the corresponding 2 : 5-compound, inasmuch as its solutions exhibited no fluorescence. Its constitution was subsequently confirmed by its conversion into mm′pp′-*tetrahydroxydiphenacylamine hydriodide*, methyl iodide, and ammonium iodide by means of hydriodic acid (p. 2523).

ω-*Chloro*-op-*dimethoxyacetophenone.*

Resorcinol dimethyl ether was prepared from resorcinol by the action of methyl sulphate and potassium hydroxide, and purified by distillation. The dimethyl ether was then dissolved in carbon disulphide, and the requisite amount of chloroacetyl chloride added. One molecular proportion of powdered aluminium chloride was then introduced, when a violent reaction ensued. After removing the solvent, the residue was treated with ice and hydrochloric acid, the resulting solid being collected and crystallised from alcohol. A very good yield of small, colourless, prismatic needles, melting at 96°, was thus obtained:

0·1233 gave 0·2518 CO_2 and 0·0577 H_2O. C=55·7; H=5·2.

$C_{10}H_{11}O_3Cl$ requires C=55·9; H=5·1 per cent.

ω-*Chloro*-op-*dimethoxyacetophenone*, $(MeO)_2C_6H_3 \cdot CO \cdot CH_2Cl$, is somewhat sparingly soluble in alcohol, but much more readily so in ethyl acetate or chloroform. It was formed in much better yield than the corresponding *mp*-compound.

Attempts to convert ω-chloro-*op*-dimethoxyacetophenone into pyrazine derivatives by heating with alcoholic ammonia resulted only in the formation of brown resins, just as was the case when ω-chloro-*o*-methoxyacetophenone was employed. It therefore appears that the presence of a methoxyl group in the ortho-position with respect to the side-chain precludes the formation of substituted pyrazines from ω-chloroacetophenone derivatives.

Attempts were made to prepare an ω-chlorotrimethoxyacetophenone by the interaction of chloroacetyl chloride and pyrogallol trimethyl ether, but without success.

ω-*Amino*-op-*dihydroxyacetophenone and its Derivatives.*

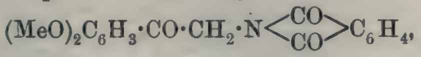
It is subsequently shown that the methoxy-2:5-diphenylpyrazines readily yield ω-aminohydroxyacetophenones, the formation of which was the primary object of this research. Since, however, no pyrazine derivative could be obtained from ω-chloro-*op*-dimethoxyacetophenone, other means had to be devised for the conversion of this compound into the desired dihydroxy-amine.

ω-Chloro-*op*-dimethoxyacetophenone was heated in a nickel crucible at about 160° with rather more than one molecular proportion of potassium phthalimide until the reaction mixture, which was at first fairly fluid, became almost solid. The product was then extracted several times with boiling xylene, and the combined filtered liquids concentrated to a small bulk. The product which separated on cooling was collected and repeatedly boiled with large quantities of water until free from phthalimide, after which it was recrystallised from xylene or glacial acetic acid, when it formed acicular crystals, melting at 188°:

0·0903 gave 0·2209 CO_2 and 0·0394 H_2O. C = 66·7; H = 4·8.

$C_{18}H_{15}O_5N$ requires C = 66·5; H = 4·6 per cent.

ω-Phthalimino-op-*dimethoxyacetophenone*,



$$(MeO)_2C_6H_3\cdot CO\cdot CH_2\cdot N<\begin{matrix}CO\\CO\end{matrix}>C_6H_4,$$

is insoluble, or very sparingly soluble, in all the usual solvents, with the exception of glacial acetic acid and boiling xylene, in which it is moderately soluble.

The above-described phthalide derivative was boiled with concentrated hydriodic acid containing some glacial acetic acid, when it very gradually passed into solution. The mixture was then diluted with water, and repeatedly extracted with ether for the removal of the phthalic acid, after which it was evaporated to dryness under diminished pressure. The solid residue was then dissolved in alcohol, the solution concentrated, ethyl acetate added, and the mixture again evaporated somewhat, when *ω-amino*-op-*dihydroxyacetophenone hydriodide*, $C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot NH_2,HI$, separated from the boiling mixture:

0·2196 gave 0·1733 AgI. I = 42·7.
0·4535 „ 0·3405 AgI. I = 42·8.

$C_8H_9O_3N,HI$ requires I = 43·0 per cent.

ω-Amino-*op*-dihydroxyacetophenone hydriodide forms nearly colourless needles, which decompose at 258°. It is readily soluble in water or alcohol, but dissolves only sparingly in ethyl acetate.

ω-Amino-op-*dihydroxyacetophenone Hydrochloride*, $C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot NH_2,HCl$.—This salt was prepared by the addition of concentrated hydrochloric acid to an alcoholic solution of the corresponding hydriodide, when the new derivative immediately separated in needles. When crystallised from water or dilute alcohol, it yielded small, hard prisms, which melted at 280°, darkening previously:

0·3297 gave 0·2292 AgCl. Cl = 17·2.

$C_8H_9O_3N,HCl$ requires Cl = 17·4 per cent.

ω-Amino-op-*dihydroxyacetophenone Aurichloride*, $C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot NH_2,HAuCl_4$.—The gold salt of ω-amino-*op*-dihydroxyacetophenone was readily soluble in water, but crystallised from its concentrated solution in orange-coloured leaflets, which, on heating, gradually darkened, and finally melted at 283°. The dried salt was analysed:

0·1201 gave 0·0467 Au. Au = 38·9.

$C_8H_9O_3N,HAuCl_4$ requires Au = 38·9 per cent.

ω-Amino-op-*dihydroxyacetophenone Platinichloride*,
$[C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot NH_2]_2,H_2PtCl_6$.
—This derivative was rather readily soluble in water, and crystallised from this solvent in fawn-coloured needles, which melted and decomposed at 247°:

0·1037 gave 0·0294 Pt. Pt = 28·5.

$(C_8H_9O_3N)_2H_2PtCl_6$ requires Pt = 28·5 per cent.

ω-Amino-op-*dihydroxyacetophenone picrate*, $C_8H_9O_3N,C_6H_3O_7N_3$, crystallised from water in bright yellow needles, which melted and decomposed at 222°.

ω-Amino-op-*dihydroxyacetophenone*, $C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot NH_2$, was prepared from the above-described hydriodide or hydrochloride by the addition of a hot concentrated solution of sodium carbonate to a similar solution of the respective salt, both liquids having previously been deprived of dissolved air by boiling. The new base then immediately separated in small, pink-coloured plates, which, on heating to 310°, suffered some decomposition, but did not melt:

0·1065 gave 0·2240 CO_2 and 0·0558 H_2O. C = 57·3; H = 5·8.

$C_8H_9O_3N$ requires C = 57·5; H = 5·4 per cent.

ω-Amino-*op*-dihydroxyacetophenone is soluble in both acids and alkali hydroxides, but is insoluble, or practically so, in all the usual solvents with the exception of pyridine, although when dissolved in the last-mentioned liquid it suffered change.

Attempts to prepare *ω-amino*-op-*dimethoxyacetophenone* by heating ω-phthalimino-*op*-dimethoxyacetophenone with hydrochloric acid were unsuccessful, as the methyl groups were partly eliminated by this treatment, the resulting product being a mixture.

oo′pp′-*Tetrahydroxy*-2 : 5-*diphenylpyrazine*.

ω-Amino-*op*-dihydroxyacetophenone was boiled with pyridine, when it slowly dissolved, the solution acquiring a yellow colour. The liquid was then concentrated and cooled, when a substance separated in yellow needles. This was collected, but when washed with ethyl acetate, or when dried, it lost pyridine of crystallisation, and became bright orange-coloured. It was unchanged at 326°, but at a higher temperature sublimed in yellow leaflets:

0·1033 gave 0·2447 CO_2 and 0·0400 H_2O. C = 64·6; H = 4·3.

$C_{16}H_{12}O_4N_2$ requires C = 64·8; H = 4·1 per cent.

This substance was evidently oo′pp′-*tetrahydroxy*-2 : 5-*diphenylpyrazine*, $C_6H_2(OH)_2\cdot C_4H_2N_2\cdot C_6H_3(OH)_2$, and had been formed by the condensation of two molecules of the original keto-base followed by spontaneous oxidation of the resulting oo′pp′-*tetrahydroxy*-

3 : 6-*dihydro*-2 : 5-*diphenylpyrazine*. It yielded unstable salts with the mineral acids, of which the *monosulphate* was bright orange and the *disulphate* intense purple. *oo′pp′*-Tetrahydroxy-2 : 5-diphenylpyrazine is very sparingly soluble in glacial acetic acid, more readily soluble in pyridine, and insoluble in all the other usual solvents.

oo′pp′-*Tetrabenzoyloxy*-2 : 5-*diphenylpyrazine*,

$$C_6H_3(OBz)_2{\cdot}C_4H_2N_2{\cdot}C_6H_3(OBz)_2.$$

—The above-described *oo′pp′*-tetrahydroxy-2 : 5-diphenylpyrazine readily underwent benzoylation when treated according to the Schotten-Baumann method, yielding a product which crystallised from ethyl acetate in glistening, colourless leaflets, melting at 212°:

0·0976 gave 0·2643 CO_2 and 0·0356 H_2O. C = 73·8; H = 4·0.

$C_{44}H_{28}O_8N_2$ requires C = 74·1; H = 3·9 per cent.

oo′pp′-*Tetrabenzoyloxy*-2 : 5-*diphenylpyrazine* is somewhat sparingly soluble in ethyl acetate and in alcohol, but dissolves readily in chloroform.

With the object of preparing the benzoyl derivative of ω-amino-*op*-dihydroxyacetophenone, the hydriodide of this base was dissolved in water, benzoyl chloride added, and then excess of aqueous potassium hydroxide introduced, and the mixture shaken for some time. The pasty product which separated was collected, dissolved in boiling absolute alcohol, and then submitted to steam distillation for the removal of the ethyl benzoate which had been formed from the occluded excess of benzoyl chloride. The non-volatile residue was dissolved in alcohol, when, on keeping, a crystalline benzoyl derivative separated, but by no means in quantitative yield. The mother liquors from this solid contained an uncrystallisable oil, which, from a subsequent observation, would appear to have been the compound which it was sought to prepare, namely, ω-*benzoylamino*-op-*dibenzoyloxyacetophenone*, $C_6H_3(OBz)_2{\cdot}CO{\cdot}CH_2{\cdot}NHBz$. The crystalline solid which was obtained formed small prisms, melting at 136—137°, and, on analysis, was found to be the benzoyl derivative of a condensation product of the base:*

0·1532 gave 0·4106 CO_2 and 0·0624 H_2O. C = 73·1; H = 4·5.

$C_{22}H_{15}O_4N$ requires C = 73·6; H = 4·2 per cent.

0·2970, in 24 of benzene, gave $\Delta t = -0·165°$. M.W. = 375.

$C_{22}H_{15}O_4N$ requires M.W. = 357.

This *compound* was therefore the dibenzoyl derivative of an internal anhydride of ω-amino-*op*-dihydroxyacetophenone, and since an analogous compound was obtained from ω-amino-*o*-hydroxyacetophenone (p. 2518), but not from the related bases containing hydroxyl groups in the *m*- or *p*-positions, it would seem likely that the *o*-hydroxyl group was concerned in the anhydride formation. In view of this consideration, it would appear probable that the substance melting at 136—137° is a dibenzoyl derivative of 6-hydroxyindoxyl (X):

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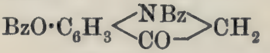
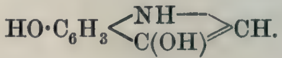
* The same compound was obtained when ω-amino-*op*-dihydroxyacetophenone hydriodide was benzoylated in pyridine solution.



$BzO\cdot C_6H_3{<}\begin{matrix}NBz\\CO\end{matrix}{>}CH_2$

(X.)



$HO\cdot C_6H_3{<}\begin{matrix}NH—\\C(OH)\end{matrix}{\geqslant}CH.$

(XI.)

6-Hydroxyindoxyl, however, might have been expected to react in its enolic form (XI), yielding a tribenzoyl derivative.

That one of the benzoyl groups was attached to nitrogen was proved by the conversion of this dibenzoyl derivative into ω-benzoylamino-*op*-dihydroxyacetophenone by the action of alkali hydroxides.

ω-Benzoylamino-op-*dihydroxyacetophenone*,

$$C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot NHBz.$$

—A quantity of the dibenzoyl derivative melting at 136—137° was boiled with concentrated alcoholic potassium hydroxide for one hour, when water was added, and the mixture acidified with hydrochloric acid. A compound then separated in slender, glistening prisms, melting and decomposing at 260—265°:

0·1339 gave 0·3267 CO_2 and 0·0590 H_2O. C = 66·5; H = 4·8.

$C_{15}H_{13}O_4N$ requires C = 66·4; H = 4·8 per cent.

ω-Benzoylamino-op-*dihydroxyacetophenone* is very sparingly soluble in alcohol, ethyl acetate, chloroform, or benzene, moderately so in glacial acetic acid, and readily so in pyridine. On prolonged heating with concentrated hydrochloric acid, it yielded ω-amino-*op*-dihydroxyacetophenone hydrochloride and benzoic acid, and on benzoylation it yielded a compound which appeared to be the *tribenzoyl* derivative of the corresponding base. This compound was a liquid, and was doubtless identical with the similar product which was obtained together with the dibenzoyl derivative melting at 136—137°, as previously noted.

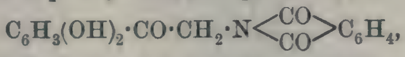
ω-Phthalimino-op-*dihydroxyacetophenone*.

During the hydrolysis of ω-phthalimino-*op*-dimethoxyacetophenone by means of hydriodic acid, it was observed that the reaction proceeded in two stages, the methyl groups being much more rapidly eliminated than was the phthalyl radicle. In one experiment, therefore, the reaction was stopped as soon as the evolution of methyl iodide had ceased, the mixture being diluted with water and cooled. A solid then separated, which was collected and washed. When recrystallised from acetic acid, this substance formed small tufts of short, colourless prisms, which gradually darkened above 250°, and fused at 270°:

0·1835 gave 0·4350 CO_2 and 0·0637 H_2O. $C=64·6$; $H=3·8$.

$C_{16}H_{11}O_5N$ requires $C=64·6$; $H=3·7$ per cent.

ω-Phthalimino-op-*dihydroxyacetophenone*,



$$C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot N{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_4,$$

is rather sparingly soluble in most solvents. When heated with concentrated hydrochloric or hydriodic acids, it yielded the corresponding amine.

ω-Phthalamino-op-*dihydroxyacetophenone*,

$$C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H.$$

—The above-described phthalimino-derivative was dissolved in aqueous potassium hydroxide, and the solution boiled for some time. The mixture was then acidified with hydrochloric acid, boiled with animal charcoal, and the filtered liquid concentrated to a small bulk and cooled. The solid which separated consisted largely of potassium chloride, but also contained crystals of an organic compound. The latter was isolated by extraction with boiling xylene, after which it was finally purified by crystallisation from water. Long, glistening leaflets were thus obtained, which melted at 227°:

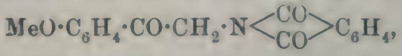
0·1372 gave 0·3064 CO_2 and 0·0519 H_2O. $C=60·9$; $H=4·2$.

$C_{16}H_{13}O_6N$ requires $C=61·0$; $H=4·1$ per cent.

Derivatives of ω-Amino-o-hydroxyacetophenone.

Since ω-chloro-*o*-methoxyacetophenone gave only resinous products when heated with ammonia, it was necessary to employ potassium phthalimide for the conversion of this chloro-ketone into the corresponding amine, just as was the case with the analogous *op*-dimethoxy-compound (compare p. 2512).

ω-Chloro-*o*-methoxyacetophenone was therefore converted into the corresponding phthalimino-derivative in a manner precisely similar to that employed in the case of the *op*-dimethoxy-derivative. The resulting *ω-phthalimino-o-methoxyacetophenone*,



$$MeO\cdot C_6H_4\cdot CO\cdot CH_2\cdot N{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_4,$$

was very sparingly soluble in most solvents, but was readily purified by crystallisation from slightly diluted acetic acid. It formed colourless, diamond-shaped plates, melting at 200·5°:

0·1553 gave 0·3972 CO_2 and 0·0632 H_2O. $C=69·5$; $H=4·5$.

$C_{17}H_{13}O_4N$ requires $C=69·2$; $H=4·4$ per cent.

This derivative was boiled for three hours with a mixture of glacial acetic acid and concentrated hydriodic acid. After freeing the liquid from phthalic acid by extraction with ether, the mixture was evaporated to dryness under diminished pressure, and the residue crystallised from a mixture of ethyl acetate and alcohol.

Very lustrous, colourless plates were thus obtained, which melted at 255°:

0·3846 gave 0·3230 AgI. I = 45·4.

$C_8H_9O_2N,HI$ requires I = 45·5 per cent.

ω-Amino-o-hydroxyacetophenone hydriodide,

$HO{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}NH_2,HI,$

is very readily soluble in water or alcohol, but only sparingly so in ethyl acetate. It does not tend to become discoloured, as is the case with salts of the analogous bases containing a hydroxyl group in the meta- or para-position with respect to the side-chain.

A quantity of this hydriodide was dissolved in pyridine and benzoylated by means of benzoyl chloride. The product crystallised readily from ethyl acetate, forming colourless plates, which melted at 133°:

0·1277 gave 0·3538 CO_2 and 0·0530 H_2O. C = 75·6; H = 4·6.

$C_{15}H_{11}O_2N$ requires C = 75·9; H = 4·7 per cent.

This compound was therefore evidently the benzoyl derivative of a condensation product of ω-amino-*o*-hydroxyacetophenone, and is doubtless constituted analogously to the corresponding derivative of the *op*-dihydroxy-base (p. 2516). It may therefore be 1-*benzoylindoxyl*, a compound which does not appear to have been prepared previously.

oo′-*Dihydroxy*-2 : 5-*diphenylpyrazine*.

A quantity of ω-amino-*o*-hydroxyacetophenone hydriodide was dissolved in water and aqueous sodium carbonate added, the resulting precipitate being collected, and crystallised from xylene. A substance was thus obtained in yellow needles, which melted at 259—262°, and were insoluble in dilute acids. The same compound was obtained if the solution of the hydriodide were rendered alkaline by means of sodium hydroxide, and then acidified, the resulting precipitate being recrystallised from xylene:

0·0904 gave 0·2420 CO_2 and 0·0400 H_2O. C = 73·0; H = 4·9.

$C_{16}H_{12}O_2N_2$ requires C = 72·7; H = 4·5 per cent.

This substance was evidently a condensation product, and its properties indicated it to be oo′-*dihydroxy*-2 : 5-*diphenylpyrazine*, $C_4H_2N_2(C_6H_4{\cdot}OH)_2$. It is very sparingly soluble or insoluble in nearly all solvents, and forms unstable salts of a bright red colour when treated with mineral acids in an anhydrous solvent. When heated above its melting point, it sublimed in yellow leaflets.

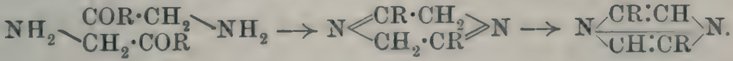
It appears from this result that ω-amino-*o*-hydroxyacetophenone, when dissolved, behaves in a manner strictly analogous to that exhibited by the *op*-dihydroxy-base. That is to say, that two molecules condense with the formation of oo′-*dihydroxy*-3 : 6-*di-*

hydro-2 : 5-*diphenylpyrazine*, which then undergoes spontaneous oxidation to the corresponding pyrazine derivative.

oo′-*Dibenzoyloxy*-2 : 5-*diphenylpyrazine*, $C_4H_2N_2(C_6H_4\cdot OBz)_2$, was prepared by benzoylating the above-described pyrazine derivative in pyridine solution. It formed small, almost colourless prisms, which melted at 185°, but the amount available was not sufficient for analysis.

Action of Hydriodic Acid on pp′-*Dimethoxy*-2 : 5-*diphenylpyrazine.*

As previously shown, the methoxy-2 : 5-diphenylpyrazines described in the present paper, which contain the substituent ether groupings in the meta- and para-positions, are formed by the condensation of two molecules of an ω-aminomethoxyacetophenone, followed by spontaneous oxidation of the resulting dihydropyrazine derivative, as follows (Gabriel, *loc. cit.*):



$$\mathrm{NH_2}\left\langle\begin{matrix}\mathrm{COR\cdot CH_2}\\\mathrm{CH_2\cdot COR}\end{matrix}\right\rangle\mathrm{NH_2}\longrightarrow\mathrm{N}\left\langle\begin{matrix}\mathrm{CR\cdot CH_2}\\\mathrm{CH_2\cdot CR}\end{matrix}\right\rangle\mathrm{N}\longrightarrow\mathrm{N}\left\langle\begin{matrix}\mathrm{CR\colon CH}\\\mathrm{CH\colon CR}\end{matrix}\right\rangle\mathrm{N}.$$

The corresponding ω-aminohydroxyacetophenones, however, could not be caused to condense under any conditions.

This behaviour is the reverse of that shown by the ortho-substituted ω-aminoacetophenones, for ω-amino-*o*-methoxyacetophenone and ω-amino-*op*-dimethoxyacetophenone will not yield pyrazines, whilst the corresponding hydroxy-derivatives spontaneously pass into such compounds.

With the object therefore of preparing *pp*′-dihydroxy-2 : 5-diphenylpyrazine, the action of hydriodic acid on *pp*′-dimethoxy-2 : 5-diphenylpyrazine was investigated. It was found, however, that this acid alone had only an extremely slow action on the compound in question, but that if a quantity of acetic acid were added to the mixture, a change ensued with moderate rapidity. The product obtained, however, was not the expected hydroxydiphenylpyrazine, but the reaction proceeded further, fission of the pyrazine nucleus taking place, resulting in the formation of two molecules of ω-amino-*p*-hydroxyacetophenone (Tutin, Caton, and Hann, *loc. cit.*). It was thus shown that the series of reactions which result in the formation of pyrazine derivatives from ω-aminoacetophenones can be quantitatively reversed by means of hydriodic acid.

A quantity of *pp*′-dimethoxy-2 : 5-diphenylpyrazine was boiled for two hours with a mixture of concentrated hydriodic and glacial acetic acids. The liquid was then diluted with water and extracted with ether for the removal of iodine, after which it was evaporated to dryness under diminished pressure. On crystallising the residue from ethyl acetate, colourless, prismatic needles were obtained, which melted at 230°:

0·3435 gave 0·2885 AgI. I = 45·4.

$C_8H_9O_2N,HI$ requires I = 45·5 per cent.

ω-Amino-p-*hydroxyacetophenone hydriodide*,

$$HO\cdot C_6H_4\cdot CO\cdot CH_2\cdot NH_2,HI,$$

is much more soluble in organic solvents than is the corresponding hydrochloride (Tutin, Caton, and Hann, *loc. cit.*). On benzoylation, it yielded ω-benzoylamino-*p*-benzoyloxyacetophenone, melting at 173—174°.

Action of Hydriodic Acid on mm′pp′-*Tetramethoxy*-2 : 5-*diphenylpyrazine.*

mm′pp′-Tetramethoxy-2 : 5-diphenylpyrazine was boiled for two hours with a mixture of glacial acetic and concentrated hydriodic acids, after which the liquid was diluted, extracted with ether, and evaporated to dryness under diminished pressure. The residue was crystallised from a mixture of ethyl acetate and alcohol, when it formed small, nearly colourless prisms, melting at 247—248°:

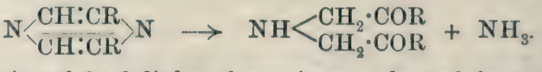
0·2175 gave 0·1717 AgI. I = 42·7.

$C_8H_9O_3N,HI$ requires I = 43·0 per cent.

This salt was therefore evidently *ω-amino*-mp-*dihydroxyacetophenone hydriodide*, $C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot NH_2,HI$. On rendering its solution alkaline with sodium carbonate, ω-amino-*mp*-dihydroxyacetophenone separated in nearly colourless leaflets, which gradually decomposed and melted above 235°. This base has previously been prepared by another method during the synthesis of epinephrine (D.R.-P. 155632), and the above-described reaction therefore affords a new means of obtaining this important compound.

Action of Hydriodic Acid on 2 : 6-*Diphenylpyrazine.*

As the action of hydriodic acid on the 2 : 5-substituted pyrazines was found to result in the complete disruption of the pyrazine ring, it was considered of interest to investigate the effect of this reagent on the analogous 2 : 6-substituted bases. It was then found that the nitrogen-containing ring was broken in this case also, in the following manner:



$$N\left\langle\begin{matrix}CH{:}CR\\CH{:}CR\end{matrix}\right\rangle N \longrightarrow NH\left\langle\begin{matrix}CH_2\cdot COR\\CH_2\cdot COR\end{matrix}\right. + NH_3.$$

A quantity of 2 : 6-diphenylpyrazine was heated for several hours with a mixture of concentrated hydriodic and glacial acetic acids. On allowing the liquid to cool, a sparingly soluble hydriodide separated. This was collected, and recrystallised from glacial acetic acid, when it formed flattened needles, which melted and decomposed at 211°. This salt proved to be *diphenacylamine hydriodide*, $(C_6H_5 \cdot CO \cdot CH_2)_2NH,HI$:

0·1981 gave 0·1217 AgI. I=33·2.

$C_{16}H_{15}O_2N,HI$ requires I=33·3 per cent.

This hydriodide was converted into the corresponding hydrochloride by treatment with hydrochloric acid in alcoholic solution, when glistening leaflets were obtained, which melted at 235°, after previously becoming red. (Found, Cl=12·4. Calc., Cl=12·3 per cent.) This salt had all the properties of diphenacylamine hydrochloride, as described by Gabriel (*loc. cit.*), and it yielded gold and platinum salts, in agreement with the similar derivatives prepared by him.

The original acid filtrate from the diphenacylamine hydriodide was evaporated to dryness under diminished pressure, and the residue crystallised from a mixture of ethyl acetate and alcohol. A colourless salt was thus obtained, which dissolved easily in water, and was readily recognised by the usual tests as ammonium iodide.

Conversion of Diphenacylamine into 2: 6-*Diphenylpyrazine.*

Both Gabriel (*loc. cit.*) and the present author (p. 2502) have obtained diphenacylamine by the interaction of ω-bromo- or chloroacetophenone and ammonia, and the present author has shown that 2: 6-diphenylpyrazine is also formed in this reaction (p. 2501). Now, since diphenacylamine results when this pyrazine derivative is heated with hydriodic acid, it appeared to the present author that the former base might be the intermediate compound in the formation of the latter by the reaction mentioned. This has been found to be the case, for, when one of the above-described salts of diphenacylamine was heated with ammonia, 2: 6-diphenylpyrazine was regenerated. It is thus seen that the change which results in the formation of 2: 6-diphenylpyrazine is capable of reversion by means of hydriodic acid, just as has been shown to be the case with the analogous 2: 5-substituted pyrazines.

A quantity of diphenacylamine hydrochloride was heated in a sealed tube for three hours at 100° with a large excess of a solution of ammonia in absolute alcohol. The reaction mixture was then evaporated to dryness, the residue extracted with benzene, and the benzene liquids evaporated. The dark-coloured residue so obtained was dissolved in a small amount of ethyl acetate, and a solution of hydrogen chloride in absolute alcohol added, when 2: 6-diphenylpyrazine monohydrochloride (m. p. 189°) separated. On treatment with alcohol, this salt dissociated, yielding 2: 6-diphenylpyrazine, melting at 90°.

It is, of course, evident that the interaction of diphenacylamine and ammonia must first result in the formation of a dihydro-2:6-diphenylpyrazine, the latter then undergoing spontaneous oxidation.

Action of Hydriodic Acid on pp′-*Dimethoxy*-2:6-*diphenylpyrazine.*

A quantity of *pp′*-dimethoxy-2:6-diphenylpyrazine was boiled for several hours with a mixture of concentrated hydriodic and glacial acetic acids. On allowing the mixture to cool, a very sparingly soluble hydriodide separated in long, colourless needles, which melted and decomposed at 251°:

0·1050 gave 0·1805 CO_2 and 0·0392 H_2O. C=46·8; H=4·1.

$C_{16}H_{15}O_4N,HI$ requires C=46·5; H=3·8 per cent.

This salt therefore was pp′-*dihydroxydiphenacylamine hydriodide*, $(HO·C_6H_4·CO·CH_2)_2NH,HI$. It was very sparingly soluble in water, and rather more soluble in alcohol, but was insoluble in cold solvents in the presence of an excess of hydriodic acid. pp′-*Dihydroxydiphenacylamine*, prepared from this salt, formed dark red crystals, but as it was very unstable it was not further investigated.

pp′-*Dihydroxydiphenacylamine Hydrochloride*,
$(HO·C_6H_4·CO·CH_2)_2NH,HCl$.
—This salt was prepared by the addition of concentrated hydrochloric acid to an alcoholic solution of the corresponding hydriodide. It crystallised from alcohol in colourless leaflets, or from water in needles, and melted at 279°. It is less soluble in alcohol than the hydriodide, but dissolves in water more readily than the latter:

0·2093 gave 0·0914 AgCl. Cl=10·8.

$C_{16}H_{15}O_4N,HCl$ requires Cl=11·0 per cent.

pp′-*Dihydroxydiphenacylamine Platinichloride*,
$[(HO·C_6H_4·CO·CH_2)_2NH]_2H_2PtCl_6$.
—This derivative crystallised very readily in buff-coloured needles, which melted and decomposed at 230°:

0·1210 gave 0·0241 Pt. Pt=19·9.

$(C_{16}H_{15}O_4N)_2H_2PtCl_6$ requires Pt=19·9 per cent.

pp′-*Dihydroxydiphenacylamine Aurichloride*,
$(HO·C_6H_4·CO·CH_2)_2NH,HAuCl_4$.
—This salt crystallised readily in bright yellow needles, which melted at 259° after undergoing some decomposition:

0·1012 gave 0·0319 Au. Au=31·5.

$C_{16}H_{15}O_4N,HAuCl_4$ requires Au=31·5 per cent.

pp′-*Dihydroxydiphenacylamine picrate*, $C_{16}H_{15}O_4N,C_6H_3O_7N_3$, forms long, bright yellow needles, which melt at 169°.

Conversion of pp′*-Dihydroxydiphenacylamine into* pp′*-Dihydroxy-2 : 6-diphenylpyrazine.*

pp′-Dihydroxydiphenacylamine hydrochloride was heated for two hours in a sealed tube at 100° with a large excess of a solution of ammonia in absolute alcohol. The mixture was then evaporated, and the residue extracted with boiling xylene. On crystallising from glacial acetic acid the material dissolved by the xylene, small, pale yellow prisms, melting at 305°, were obtained:

0·1210 gave 0·3192 CO_2 and 0·0496 H_2O. C = 72·5 ; H = 4·5.

$C_{16}H_{12}O_2N_2$ requires C = 72·7 ; H = 4·5 per cent.

This compound was evidently pp′*-dihydroxy*-2 : 6-*diphenylpyrazine*, $C_4H_2N_2(C_6H_4{\cdot}OH)_2$. It yielded unstable salts with the mineral acids, the *monohydrochloride* and *monosulphate* being orange-coloured, whilst the *disulphate* was deep reddish-purple.

Action of Hydriodic Acid on mm′pp′*-Tetramethoxy-2 : 6-diphenylpyrazine.*

mm′*pp*′-Tetramethoxy-2 : 6-diphenylpyrazine was heated with hydriodic acid in a manner similar to that described in connexion with the corresponding dimethoxy-compound. A hydriodide was thus obtained, which crystallised from acetic acid in colourless leaflets, and melted and decomposed at 236°:

0·1725 gave 0·0918 AgI. I = 28·3.

$C_{16}H_{15}O_6N,HI$ requires I = 28·5 per cent.

mm′pp′*-Tetrahydroxydiphenacylamine hydriodide*,

$$[C_6H_3(OH)_2{\cdot}CO{\cdot}CH_2]_2NH,HI,$$

is somewhat more soluble in water than the corresponding dihydroxy-compound. On treating its aqueous solution with alkalis, a yellow colour is produced, but oxidation very rapidly ensues, with the development of a brown colour.

mm′pp′*-Tetrahydroxydiphenacylamine Hydrochloride*,

$$[C_6H_3(OH)_2{\cdot}CO{\cdot}CH_2]_2NH,HCl.$$

—This salt was prepared by the addition of concentrated hydrochloric acid to an alcoholic solution of the above-described hydriodide, when the new derivative immediately separated. It crystallises from water in colourless leaflets, which melt and decompose at 264°:

0·2687 gave 0·1075 AgCl. Cl = 9·9.

$C_{16}H_{15}O_6N,HCl$ requires Cl = 10·0 per cent.

On treating a solution of mm′pp′*-tetrahydroxydiphenacylamine hydrochloride* with auric or platinic chloride, the respective metal was quickly deposited. A *mercurichloride* was obtained from the hydrochloride in tufts of small, white needles, but it was unstable, and, on warming its solution, mercurous chloride soon separated.

mm′pp′-*Tetrahydroxydiphenacylamine picrate*,

$$[C_6H_3(OH)_2\cdot CO\cdot CH_2]_2NH,C_6H_3O_7N_3,$$

crystallised readily in tufts of yellow needles, which contained water of crystallisation, and, when air dried, melted at 112—115°.

In conclusion, the author wishes to acknowledge his indebtedness to Mr. F. W. Caton, B.A., B.Sc., for the preparation and purification of the ω-chloro-*o*- and *p*-methoxyacetophenones employed in this research.

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CCLVIII.—*The Absorption Spectra of Some Substituted Pyrazines and their Salts.*

By FRANK TUTIN and FREDERIC WILLIAM CATON.

IN the preceding paper, the preparation of 2:5- and 2:6-diphenylpyrazine, *pp*′-dimethoxy-2:5- and -2:6-diphenylpyrazine, and *mm*′*pp*′-tetramethoxy-2:5- and -2:6-diphenylpyrazine is described. During the course of this work, certain remarkable colour changes were observed on treating these bases with acids, which suggested to us that a fuller investigation of the subject might lead to interesting results. Thus, whilst the hydrochloride of 2:6-diphenylpyrazine appeared colourless, the corresponding salts of the analogous *pp*′-dimethoxy- and *mm*′*pp*′-tetramethoxy-bases were bright yellow and orange-coloured respectively. Furthermore, on adding sulphuric acid to a chloroform solution of *pp*′-dimethoxy-2:5-diphenylpyrazine, a yellow liquid which exhibited an intense, green fluorescence was first produced, whilst on the addition of an excess of the acid a very deep violet-coloured solution resulted.

The further investigation of the bases in question rendered it evident that pyrazine derivatives, which have hitherto been stated to be monoacidic bases, in reality yield two series of salts, the di-acid salts being in all cases much more highly coloured than the corresponding derivatives containing but one equivalent of acid. The depth of colour of corresponding salts of analogous bases was found to increase with the accumulation of methoxyl groups, and to be somewhat greater in compounds of the 2:5-series than in the corresponding members of the 2:6-series.

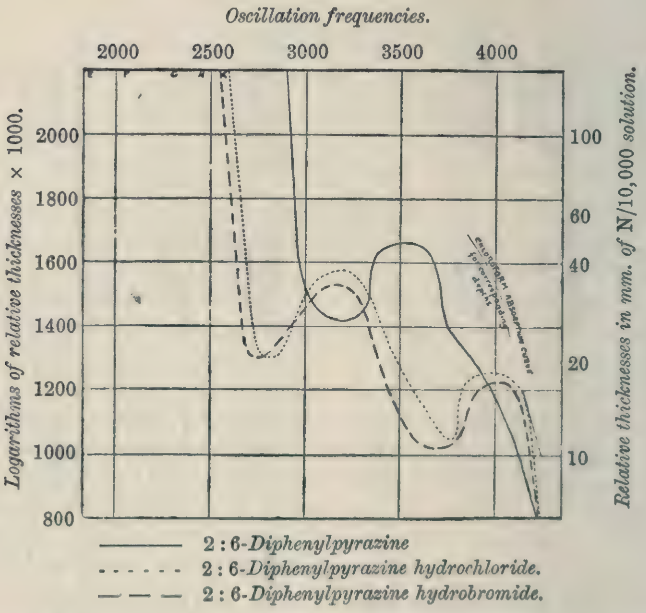
The colours of the salts obtained will be seen on reference to the following table:

Base.	Mono-hydrochloride.	Mono-hydrobromide.	Monosulphate.	Dihydro-chloride.	Dihydrobromide.	Disulphate.
2 : 5-Diphenylpyrazine.	Very pale yellow solution.	Pale yellow solution.	(?)	Bright yellow solution.	Golden-yellow crystals.	Yellow crystals.
2 : 6-Diphenylpyrazine.	Practically colourless crystals.	Pale yellow crystals.	Colourless crystals.	Yellow solution.	(?)	Yellow solution.
pp'-Dimethoxy-2 : 5-diphenylpyrazine.	Bright yellow crystals.	Orange-coloured crystals.	Yellow crystals.	(?)	Deep violet solution, or deep violet solid (HBr and solid base).	Crystals resembling potassium permanganate
pp'-Dimethoxy-2 : 6-diphenylpyrazine.	Yellow crystals.	Deep yellow crystals.	Pale yellow crystals.	(Could not be formed.)	Deep violet solid (HBr and solid base).	Violet-coloured solution.
mm'pp'-Tetramethoxy-2 : 5-diphenylpyrazine.	—	—	Orange-red crystals.	—	—	Deep blue solution, or black crystals with metallic lustre
mm'pp'-Tetramethoxy-2 : 6-diphenylpyrazine.	Deep yellow crystals.	Orange-coloured crystals.	Yellow crystals.	(Could not be formed.)	Bluish-black solid (HBr and solid base).	Deep blue solution.

In order therefore to throw some light on the nature of these colour changes, some of the above-mentioned bases and certain of their salts have been examined spectroscopically in chloroform solution. This solvent was chosen as both the bases and their salts are sufficiently soluble in it, and, although it has a certain amount of general absorption in the extreme ultra-violet region of the spectrum, it was thought that it would not interfere appreciably with the results. Moreover, the salts of the pyrazines have much less tendency to hydrolyse when dissolved in chloroform than in alcoholic solution.*

The curves obtained from 2 : 6-diphenylpyrazine, *pp′*-dimethoxy-2 : 6-diphenylpyrazine, and *mm′pp′*-tetramethoxy-2 : 6-diphenylpyrazine are shown in Figs. 1, 2, and 3 respectively. From these it is seen that each of the bases shows absorption in the ultra-violet part of the spectrum, and that salt-formation is accompanied by a considerable shift of the bands towards the red end, thus accounting for the development of colour on treatment with acids. In the case of 2 : 6-diphenylpyrazine hydrochloride, which is practically colourless, the absorption bands still lie within the ultra-violet

FIG. 1.



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* Even when employing chloroform as a solvent for the salts it was necessary to have a certain excess of the respective acid in the solution.

FIG. 2.

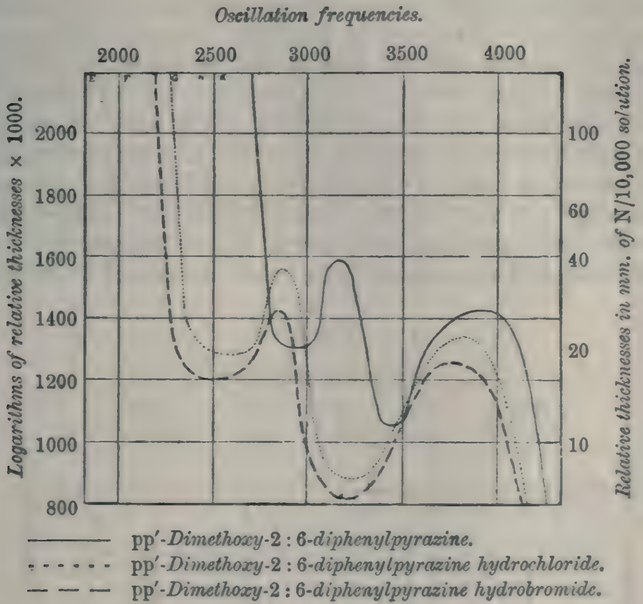
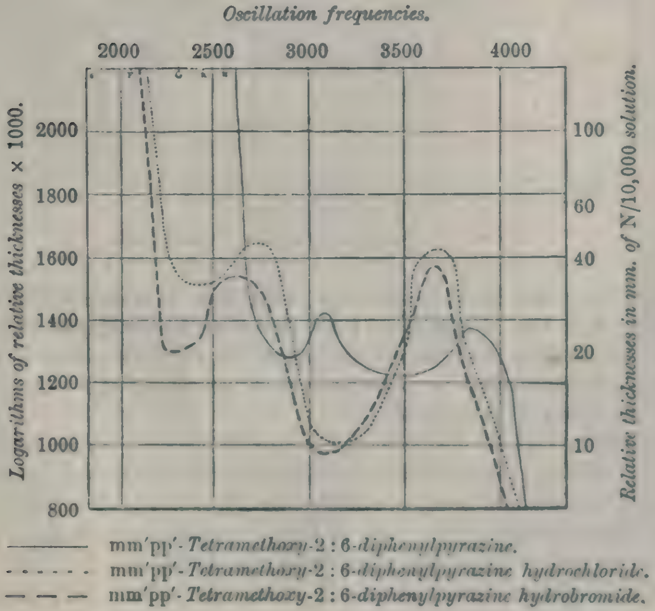

Oscillation frequencies.
2000
2500
3000
3500
4000
E
F
G
h
K
Logarithms of relative thicknesses × 1000.
2000
1800
1600
1400
1200
1000
800
Relative thicknesses in mm. of N/10,000 solution.
100
60
40
20
10
pp′-Dimethoxy-2 : 6-diphenylpyrazine.
pp′-Dimethoxy-2 : 6-diphenylpyrazine hydrochloride.
pp′-Dimethoxy-2 : 6-diphenylpyrazine hydrobromide.

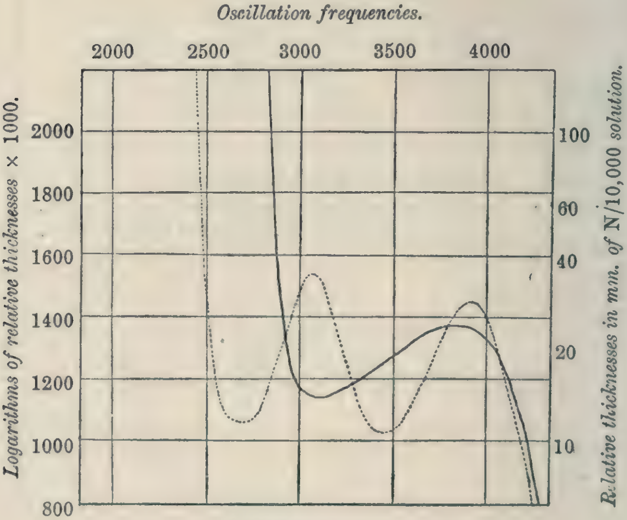
FIG. 3.


Oscillation frequencies.
2000
2500
3000
3500
4000
E
F
G
h
K
Logarithms of relative thicknesses × 1000.
2000
1800
1600
1400
1200
1000
800
Relative thicknesses in mm. of N/10,000 solution.
100
60
40
20
10
mm′pp′-Tetramethoxy-2 : 6-diphenylpyrazine.
mm′pp′-Tetramethoxy-2 : 6-diphenylpyrazine hydrochloride.
mm′pp′-Tetramethoxy-2 : 6-diphenylpyrazine hydrobromide.

region, but one band shown by the corresponding hydrobromide just extends into the visible part of the spectrum, thus explaining the pale yellow colour of the salt in question. The shift of the absorption bands towards the red end of the spectrum caused by the substitution of hydrobromic for hydrochloric acid is not nearly so great as that caused by the conversion of the base into its hydrochloride, thus indicating that the alteration in position of the bands in the latter case must be due chiefly to salt-formation, and only in a minor degree to the weight or nature of the acid radicle attached.

The di- and tetra-methoxy-bases of the 2 : 6-series, and all of the salts show two absorption bands, but in the case of 2 : 6-diphenylpyrazine only one band is seen. Nevertheless, it is considered most probable that the absorption of all three 2 : 6-substituted bases is, in reality, similar, the second absorption band of the last-mentioned base being lost owing to the absorption shown by the chloroform which was used as a solvent.

FIG. 4.



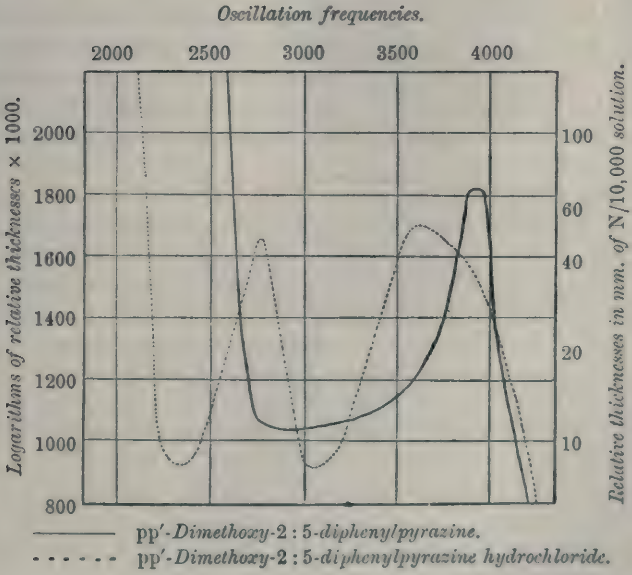
——— 2 : 5-*Diphenylpyrazine.*

- - - - - - 2 : 5-*Diphenylpyrazine hydrochloride.*

The curves yielded by 2 : 5-diphenylpyrazine and its monohydrochloride, and by *pp*′-dimethoxy-2 : 5-diphenylpyrazine and the corresponding salt of this base, are shown in Figs. 4 and 5 respectively. It will be observed in the case of these 2 : 5-substituted bases that the curves show only one absorption band, whilst two such are exhibited by the curves obtained from the salts. One possible explanation of this is that the second absorption band of the 2 : 5-substituted bases has been lost owing to the absorption caused by the chloroform, just as is thought likely to be the case with 2 : 6-diphenylpyrazine, as already mentioned. On the other hand, the fact that the band shown by the 2 : 5-substituted bases is much broader than either of the bands in any of the other curves obtained would suggest that in the bases of the 2 : 5-series the two absorption bands may have become merged into one.

Certain general conclusions may be drawn from the absorption curves given, namely, the following: (1) The similarity of the curves given by the bases and their salts, particularly in the 2 : 6-series, indicates that no change other than the rearrangement of valencies necessitated by the change $N^{III} \longrightarrow N^{V}$ occurs on treating the bases in question with acids. (2) That salt-formation causes an increased persistency of the bands, together with a very large shift towards the red end of the spectrum. This result is similar to, but very much greater than, that which has previously been observed in the case of pyridine and its homologues (Hartley, Trans., 1885, **47**, 685; Baker and Baly, *ibid.*, 1907, **91**, 1122; and Purvis, *Proc. Camb. Phil. Soc.*, 1908, **14**, 436). (3) The introduction of methoxyl groups causes a shift of the absorption bands towards the red end of the spectrum—an effect which has several times pre-

FIG. 5.



viously been noted by other workers. (4) The position of the substituent groups in the pyrazine nucleus affects the position of the absorption bands shown by the bases and their salts, the bands shown by the 2:5-substituted compounds being nearer the red end of the spectrum than those shown by their 2:6-substituted isomerides (compare Purvis, *loc. cit.*).

The absorption curves given also appear to indicate that the weight of the acid radicle present in a given salt had an effect on the position of the bands, the hydrobromides being more deeply coloured than the corresponding hydrochlorides. It would appear premature, however, to consider this conclusion as proved, without considerable further evidence obtained by the study of a variety of salts, for, in every case where the sulphates could be obtained, they were found to be less deeply coloured than even the corresponding hydrochlorides, but their absorption spectra were not examined. It thus appears that the nature of the acid employed may have a greater effect than its molecular weight on the colour of the resulting salt.

The formation and properties of the salts which were obtained from the pyrazine derivatives under consideration are described below. In most cases the melting points of these derivatives were indefinite, and of no value for the purpose of characterisation.

Salts of 2:5-*Diphenylpyrazine*.—No salt of this base with one equivalent of an acid could be obtained in the solid state, but the *dihydrobromide* and *disulphate* crystallised readily. On passing hydrogen chloride into a chloroform solution of the base, a yellow liquid was obtained, which doubtless contained the *dihydrochloride*.

Dry hydrogen bromide was passed into a solution of 2:5-diphenylpyrazine in glacial acetic acid, and the mixture kept a few hours. Golden-yellow crystals then separated, which were found to be 2:5-diphenylpyrazine dihydrobromide, $C_4H_2N_2(C_6H_5)_2,2HBr$:

0·1527 gave 0·1435 AgBr. HBr = 40·5.

$C_{16}H_{12}N_2,2HBr$ requires HBr = 41·1 per cent.

This salt was readily dissociated by water, alcohol, or moist air. On heating it with ethyl acetate, it dissolved and partly dissociated, and, on cooling the solution, a mixture of dihydrobromide and base separated, but no monohydrobromide was obtained.

2:5-*Diphenylpyrazine disulphate*, $C_4H_2N_2(C_6H_5)_2,2H_2SO_4$, resulted on the addition of concentrated sulphuric acid to a solution of the respective base in ethyl acetate or glacial acetic acid; the monosulphate could not be obtained. 2:5-Diphenylpyrazine disulphate forms yellow plates, which, when exposed to moist air, readily dissociate, yielding the colourless base:

0·2417 gave 0·2570 $BaSO_4$. $H_2SO_4=44·7$.

$C_{16}H_{12}N_2,2H_2SO_4$ requires $H_2SO_4=45·8$ per cent.

Although the result of this analysis is not in very close agreement with the theoretical figures, owing to the readiness with which the salt dissociates, it nevertheless proves conclusively that the salt has the formula indicated above.

Salts of 2 : 6-*Diphenylpyrazine.*—The monohydrochloride of this base is described in the preceding paper (p. 2501). It is a practically colourless, crystalline solid. The *monohydrobromide*, however, is pale yellow, whilst the *monosulphate* is quite colourless. The *dihydrochloride* and *disulphate* were obtained in the form of solutions, both of which were yellow, but no positive indication of the formation of a dihydrobromide could be obtained.

2 : 6-*Diphenylpyrazine monohydrobromide*, $C_4H_2N_2(C_6H_5)_2,HBr$, separated in pale yellow needles on passing hydrogen bromide into a solution of the respective base in a mixture of ethyl acetate and alcohol. Like the previously described salts, it readily dissociated:

0·1408 gave 0·0840 AgBr. HBr = 25·7.

$C_{16}H_{12}N_2,HBr$ requires HBr = 25·9 per cent.

2 : 6-*Diphenylpyrazine monosulphate*, $C_4H_2N_2(C_6H_5)_2,H_2SO_4$, crystallised in quite colourless needles on adding concentrated sulphuric acid to a solution of 2 : 6-diphenylpyrazine in glacial acetic acid:

0·1316 gave 0·0934 $BaSO_4$. $H_2SO_4=29·8$.

$C_{16}H_{12}N_2,H_2SO_4$ requires $H_2SO_4=29·7$ per cent.

Salts of pp′-*Dimethoxy*-2 : 5-*diphenylpyrazine.*—The *monohydrochloride*, *monohydrobromide*, and *monosulphate* of *pp′*-dimethoxy-2 : 5-diphenylpyrazine crystallised readily, and the *disulphate* was also obtained in crystals, although it was very unstable. A solution of the *dihydrobromide* was obtained as a deep violet-coloured liquid by saturating a solution of *pp′*-dimethoxy-2 : 5-diphenylpyrazine in glacial acetic acid with hydrogen bromide; and this salt also appeared to be formed on passing dry hydrogen bromide over the solid base. No positive evidence of the formation of a dihydrochloride could be obtained.

pp′-*Dimethoxy*-2 : 5-*diphenylpyrazine monohydrochloride*,

$C_4H_2N_2(C_6H_4{\cdot}OMe)_2,HCl$,

was formed by saturating a warm solution of the pyrazine derivative in glacial acetic acid with hydrogen chloride. On cooling, the salt separated in bright yellow needles:

0·3191 gave 0·1374 AgCl. HCl = 10·9.

$C_{18}H_{16}O_2N_2,HCl$ requires HCl = 11·1 per cent.

This salt dissociated much more readily than the corresponding derivative of the 2:6-substituted base, and, when dissolved in chloroform, exhibits an intense green fluorescence.

pp′-*Dimethoxy*-2:5-*diphenylpyrazine monohydrobromide*,

$C_4H_2N_2(C_6H_4{\cdot}OMe)_2,HBr$,

was prepared in a manner similar to the salt last described. It formed orange-coloured needles:

0·2781 gave 0·1373 AgBr. HBr = 21·3.

$C_{18}H_{16}O_2N_2,HBr$ requires HBr = 21·7 per cent.

pp′-Dimethoxy-2:5-diphenylpyrazine monohydrobromide, like the corresponding hydrochloride, is fluorescent in chloroform solution.

pp′-*Dimethoxy*-2:5-*diphenylpyrazine monosulphate*,

$C_4H_2N_2(C_6H_4{\cdot}OMe)_2,H_2SO_4$,

separated in yellow needles on adding sulphuric acid to a warm solution of the respective base in glacial acetic acid, and cooling the mixture. It dissociates readily, and, like the last-mentioned two salts, is fluorescent in chloroform solution:

0·2700 gave 0·1581 $BaSO_4$. H_2SO_4 = 24·6.

$C_{18}H_{16}O_2N_2,H_2SO_4$ requires H_2SO_4 = 25·1 per cent.

When to a solution of *pp*′-dimethoxy-2:5-diphenylpyrazine in chloroform, concentrated sulphuric acid was added, a yellow solution of the monosulphate was first formed, which exhibited a brilliant green fluorescence, but on introducing an excess of the acid the base was dissolved by the latter, yielding an intensely violet-coloured liquid below the chloroform. Sufficient ethyl acetate was then added to render the mixture homogeneous, and the liquid kept a few hours, when pp′-*dimethoxy*-2:5-*diphenylpyrazine disulphate*, $C_4H_2N_2(C_6H_4{\cdot}OMe)_2,2H_2SO_4$, separated in small prisms, resembling in colour crystals of potassium permanganate. This disulphate is very unstable; it dissociates in ordinary air, yielding the yellow monosulphate, and, if the air be unusually damp, complete dissociation ensues. The dissociated mixture may, however, be successively reconverted into the yellow monosulphate and the deep violet-coloured disulphate by desiccation:

0·1224 gave 0·1200 $BaSO_4$. H_2SO_4 = 41·1.

$C_{18}H_{16}O_2N_2,2H_2SO_4$ requires H_2SO_4 = 40·2 per cent.

This disulphate dissociated so readily that it could not be washed with any solvent, and it is owing to this fact that the analysis indicated a somewhat high percentage of sulphuric acid.

Salts of pp′-*Dimethoxy*-2:6-*diphenylpyrazine*.—This base readily yielded a crystalline monohydrochloride, monohydrobromide, and *monosulphate*, the first of which has been described in the preceding paper (p. 2506). No indication of the formation of a dihydrochloride could be obtained, but the *dihydrobromide* was obtained as a very deep violet-coloured solid by passing dry hydrogen bromide over the solid base. A deep violet-coloured solution of the *disulphate* in concentrated sulphuric acid was formed, but this salt could not be crystallised.

pp′-*Dimethoxy*-2 : 6-*diphenylpyrazine monohydrobromide*,

$C_4H_2N_2(C_6H_4{\cdot}OMe)_2,HBr$,

crystallised in deep yellow needles on the addition of a little concentrated hydrobromic acid to a solution of the base in a mixture of ethyl acetate and alcohol:

0·1685 gave 0·0832 AgBr. HBr = 21·3.

$C_{18}H_{16}O_2N_2,HBr$ requires HBr = 21·7 per cent.

This salt is not fluorescent, thus differing from its 2 : 5-substituted isomeride.

pp′-*Dimethoxy*-2 : 6-*diphenylpyrazine monosulphate*,

$C_4H_2N_2(C_6H_4{\cdot}OMe)_2,H_2SO_4$,

was obtained on adding concentrated sulphuric acid to a solution of the respective base in ethyl acetate. It was not fluorescent, and formed pale yellow needles, which dissociated fairly readily:

0·2635 gave 0·1549 $BaSO_4$. H_2SO_4 = 24·7.

$C_{18}H_{16}O_2N_2,H_2SO_4$ requires H_2SO_4 = 25·1 per cent.

Salts of mm′pp′-*Tetramethoxy*-2 : 5-*diphenylpyrazine*. — The amount of this base available was very small, and therefore only its behaviour towards sulphuric acid was investigated. It was markedly more basic than the previously mentioned bases. When treated with a small amount of sulphuric acid in glacial acetic acid solution, it yielded mm′pp′-*tetramethoxy*-2 : 5-*diphenylpyrazine monosulphate*, $C_6H_3(OMe)_2{\cdot}C_4H_2N_2{\cdot}C_6H_3(OMe)_2,H_2SO_4$, which formed orange-red needles. If, however, the solution contained any excess of sulphuric acid, the orange-coloured crystals of the monosulphate soon gave place to small, jet-black prisms of the corresponding *disulphate*, $C_6H_3(OMe)_2{\cdot}C_4H_2N_2{\cdot}C_6H_3(OMe)_2,2H_2SO_4$. These crystals possessed a brilliant metallic lustre, and were permanent in the air, although they were dissociated fairly readily by alcohol. A dilute solution of *mm′pp′*-tetramethoxy-2 : 5-diphenylpyrazine disulphate in concentrated sulphuric acid had an intensely blue colour. The amount of these salts was not sufficient for analysis.

Salts of mm′pp′-*Tetramethoxy*-2 : 6-*diphenylpyrazine*.—This base readily yielded a crystalline monohydrochloride, monohydrobromide, and monosulphate, but no di-acid salt of it could be crystallised. No evidence of the existence of a dihydrochloride could be obtained, but a compound of a bluish-black colour with a bronze lustre, which was doubtless the *dihydrobromide*, was obtained by passing dry hydrogen bromide over the crystalline base. A deep blue-coloured solution of the *disulphate* in concentrated sulphuric acid was also obtained.

mm′pp′-Tetramethoxy-2 : 6-diphenylpyrazine monohydrochloride has been described in the preceding paper (p. 2511). It is deep yellow, and does not dissociate so readily as the previously described hydrochlorides.

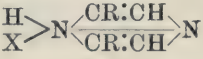
mm′pp′-*Tetramethoxy*-2 : 6-*diphenylpyrazine monohydrobromide*, $C_6H_3(OMe)_2\cdot C_4H_2N_2\cdot C_6H_3(OMe)_2,HBr$, was obtained in orange-coloured needles on passing hydrogen bromide into a solution of the respective base in warm ethyl acetate. The amount of product available was small, and it was not analysed.

mm′pp′-*Tetramethoxy*-2 : 6-*diphenylpyrazine monosulphate*,

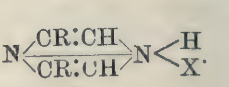
$$C_6H_3(OMe)_2\cdot C_4H_2N_2\cdot C_6H_3(OMe)_2,H_2SO_4,$$

was prepared by adding concentrated sulphuric acid to a solution of the respective base in ethyl acetate. It formed yellow needles, which were stable in the air, but were dissociated by alcohol or water.

Two series of isomeric mono-acid salts of the 2 : 6-substituted pyrazines are possible, which would be represented respectively by the following formulæ:



(I.)



(I

Throughout the course of this work, however, no indication of the presence of isomerides was observed, and it is therefore probable that the acid attaches itself to one of the nitrogen atoms more readily than to the other. If this be the case, the mono-acidic salts of the 2 : 6-substituted pyrazines are probably represented by formula II. Furthermore, the fact that no di-acid salt of the last-mentioned bases could be crystallised may be due to these salts being difficult of formation, owing to steric hindrance, but it is quite likely that it is due only to their being more soluble than their 2 : 5-substituted isomerides.

In conclusion, the authors wish to acknowledge their indebtedness to Dr. J. T. Hewitt, who kindly placed at their disposal the spectroscope with which the curves given in this paper were obtained.

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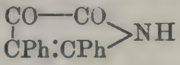
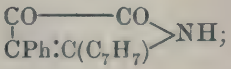
CCLIX.—*The Absorption Spectra of Various Diketopyrroline Compounds.*

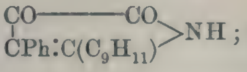
By JOHN EDWARD PURVIS.

A SERIES of coloured diketopyrrolines have been described by Ruhemann (Trans., 1909, **95**, 984, 1603; this vol., pp. 462, 1438), and it appeared to be of some interest to study these compounds in relation to their absorption and constitution; the aim of this communication is to show how far the absorption is connected with (1) the ketonic groups, (2) the replacement of the oxygen of the ketonic groups, and (3) the replacement of hydrogen of the aromatic side-chains by various groups.

N/1000-alcoholic solutions of the following substances were examined. The method of examination has been described before.

2 : 3-Diketo-4 : 5-diphenylpyrroline,  $\left.\begin{array}{l}CO{-}CO\\ |\\ CPh{:}CPh\end{array}\right>NH$; dark red.

2:3-Diketo-4-phenyl-5-tolylpyrrolines (*o*-, *m*-, *p*-),  $\left.\begin{array}{l}CO{-}CO\\ |\\ CPh{:}C(C_7H_7)\end{array}\right>NH$; dark red.

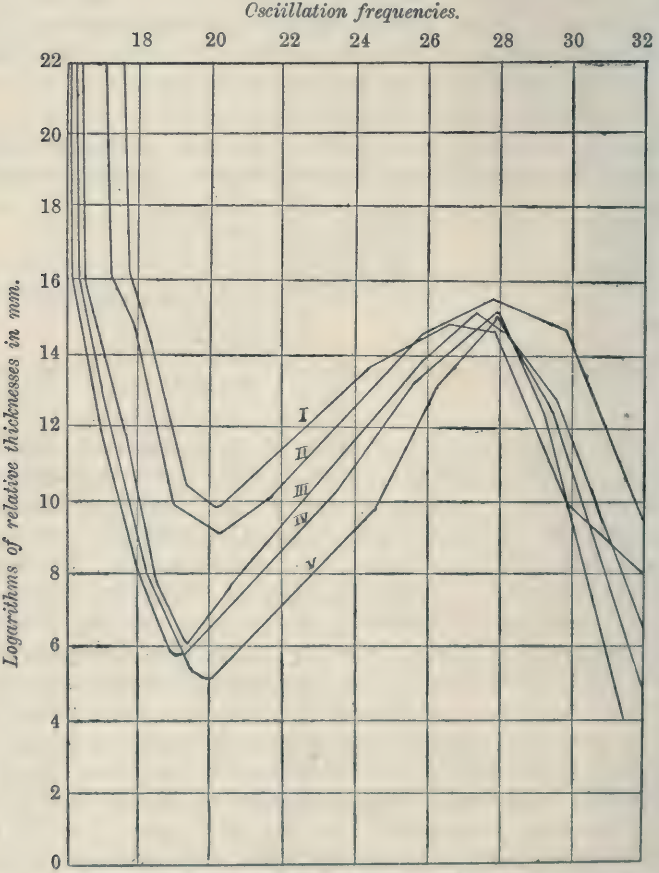
2 : 3-Diketo-4-phenyl-5-*p*-cumylpyrroline,  $\left.\begin{array}{l}CO{-}CO\\ |\\ CPh{:}C(C_9H_{11})\end{array}\right>NH$; dark red.

From the absorption curves (Fig. 1), it is evident that the absorptions are all of the same type. The differences correspond with differences in the shades of red of the different compounds. For example, the ortho-tolyl compound (I) is not quite so dark red as the meta- (III) and para- (V) compounds, and the curves show these differences, in that the rays are transmitted through greater thicknesses of the solution. It is noticeable, also, that the diphenyl compound (II) is a shade darker red than the ortho-tolyl compound, and not so deep red as the meta- and para-compounds. This is also clear from the curves, for the rays are transmitted through greater thicknesses than either the meta- or para-tolyl compounds. Or, to put it another way, the absorption band of the ortho-tolyl compound is not so strong as that of either the meta- or para-tolyl compound; and the absorption band of the diphenyl compound is a little stronger than that of the ortho-tolyl compound, but not so strong as the bands of the meta- or para-methyl derivatives.

N/10,000-solutions of the substances were also examined, but no bands were observed in the ultra-violet regions. The positions when general absorption begin, expressed in oscillation frequencies, are:

Diketodiphenylpyrroline	30 mm. thick	3246
,, ,, ,,	10 ,, ,,	3997
Diketo-*o*-tolylpyrroline	30 ,, ,,	3603
,, ,, ,,	10 ,, ,,	4199
Diketo-*m*-tolylpyrroline	30 ,, ,,	3320
,, ,, ,,	10 ,, ,,	3981
Diketo-*p*-tolylpyrroline	33 ,, ,,	3148
,, ,, ,,	10 ,, ,,	3965
Diketo-*p*-cumylpyrroline	30 ,, ,,	3153
,, ,, ,,	10 ,, ,,	3593

FIG. 1.

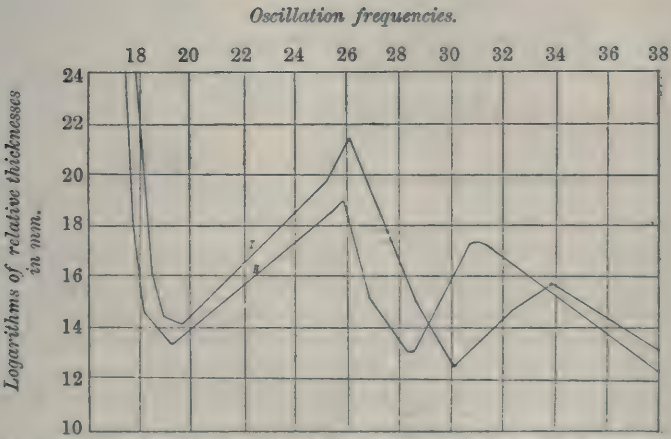


I. N/1000-*alcoholic solution of* 2 : 3 *diketo-4-phenyl-5-o-tolylpyrroline.*
II. N/1000-*alcoholic* ,, *diketodiphenylpyrroline.*
III. N/1000-*alcoholic* ,, 2 : 3-*diketo-4-phenyl-5-*m-*tolylpyrroline.*
IV. N/1000-*alcoholic* ,, 2 : 3-*diketo-4-phenyl-5-*p-*cumylpyrroline.*
V. N/1000-*alcoholic* ,, 2 : 3-*diketo-4-phenyl-5-*p-*tolylpyrroline.*

Therefore the result of the substitution of hydrogen by an aliphatic group in an aromatic side-chain does not fundamentally alter either the colour or the absorption. The observed band corresponds in each case with the colour, and there is no band produced in the ultra-violet region.

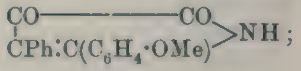
When the two diketo-groups are still left intact, and the substitution in an aromatic side-chain is by the methoxy- or methylenedioxy-groups, the dark red colour remains unchanged, but another band in the ultra-violet region is produced. The formulæ of these two derived substances are:

Fig. 2.



I. N/10,000-*alcoholic solution of* 2 : 3-*diketo*-4-*phenyl*-5-p-*anisylpyrroline*.
II. N/10,000-*alcoholic* ,, 2 : 3-*diketo*-4-*phenyl*-5-*piperonylpyrroline*.

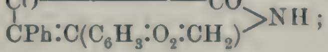
2 : 3-Diketo-4-phenyl-5-*p*-anisylpyrroline,



$$\left.\begin{array}{l}\mathrm{CO}\text{————————}\mathrm{CO}\\ |\\ \mathrm{CPh{:}C(C_6H_4{\cdot}OMe)}\end{array}\right>\mathrm{NH};$$

dark red.

2 : 3-Diketo-4-phenyl-5-piperonylpyrroline,

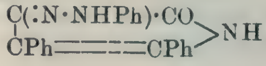


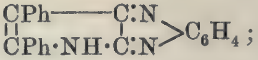
$$\left.\begin{array}{l}\mathrm{CO}\text{————————}\mathrm{CO}\\ |\\ \mathrm{CPh{:}C(C_6H_3{:}O_2{:}CH_2)}\end{array}\right>\mathrm{NH};$$

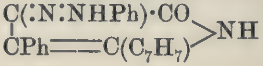
dark red.

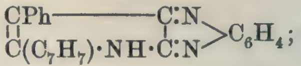
N/10,000-solutions were examined, and from the curves (Fig. 2) it will be seen that each substance has two bands. The less refrangible band of each corresponds with the bands of the previous substances. On the other hand, the more refrangible bands have no corresponding bands in the original diphenyl compounds, and they also differ from each other both in position and persistency. In other words, neither the original colour nor the corresponding absorption is fundamentally altered by the introduction of a methoxy- or a methylenedioxy-group in an aromatic side-chain, but another band is produced in the ultra-violet region corresponding with the new type of side-chain.

Further, the phenylhydrazones of the diphenyl compound and of the *p*-tolyl compound were examined in *N*/10,000-solutions. The constitutional formulæ of these substances are:

Diketodiphenylpyrrolinephenylhydrazone, 
$\begin{array}{l}\mathrm{C(:N\cdot NHPh)\cdot CO}\\ \mathrm{CPh{=\!=\!=}CPh}\end{array}\!>\mathrm{NH}$; carmine-red.

Diphenylpyrrolinophenazine, 
$\begin{array}{l}\mathrm{CPh{-\!-}C:N}\\ \mathrm{CPh\cdot NH\cdot C:N}\end{array}\!>\mathrm{C_6H_4}$; lemon-yellow.

Diketophenyl-*p*-tolylpyrrolinephenylhydrazone, 
$\begin{array}{l}\mathrm{C(:N:NHPh)\cdot CO}\\ \mathrm{CPh{=\!=}C(C_7H_7)}\end{array}\!>\mathrm{NH}$; carmine-red.

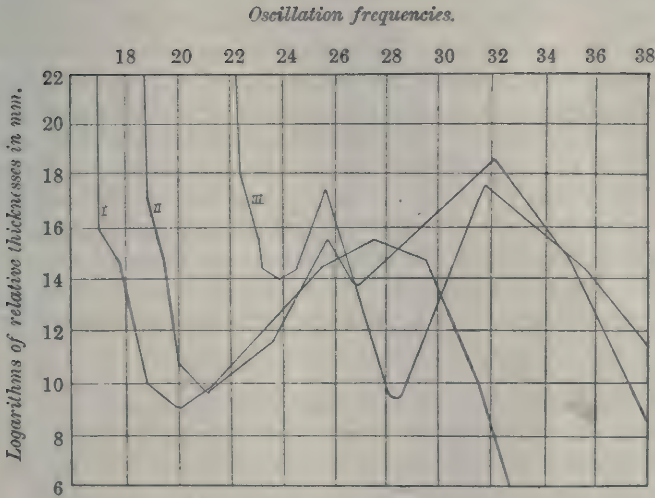
Phenyl-*p*-tolylpyrrolinophenazine, 
$\begin{array}{l}\mathrm{CPh{-\!-\!-}C:N}\\ \mathrm{C(C_7H_7)\cdot NH\cdot C:N}\end{array}\!>\mathrm{C_6H_4}$; lemon-yellow.

Considering the carmine-red phenylhydrazones, it will be seen from the curves (Fig. 3 and 4) that they show two bands. The less refrangible band corresponds with the single band of the original unsubstituted diketopyrrolines slightly shifted towards the more refrangible side; and the smaller, more refrangible one results from the introduction of the hydrazine radicle in place of oxygen of one of the ketonic groups. Considering the yellow-coloured phenazine compounds, the curves also show two bands, a smaller, less refrangible one, and a stronger one in the more refrangible side. That is to say, the successive elimination of the oxygen of both the ketonic groups produces a change in colour from dark red, through carmine-red to yellow; a decrease in the intensity of the band of the original diketonic substances; and the production of another band on the more refrangible side, the intensity of which increases by the successive elimination of the ketonic groups. It is important to notice that the increased weight of the molecule does not shift the band or the general absorption towards the red end, as is usually the case. On the contrary, the shift is towards the more refrangible end of the spectrum.

General Results and Discussion.

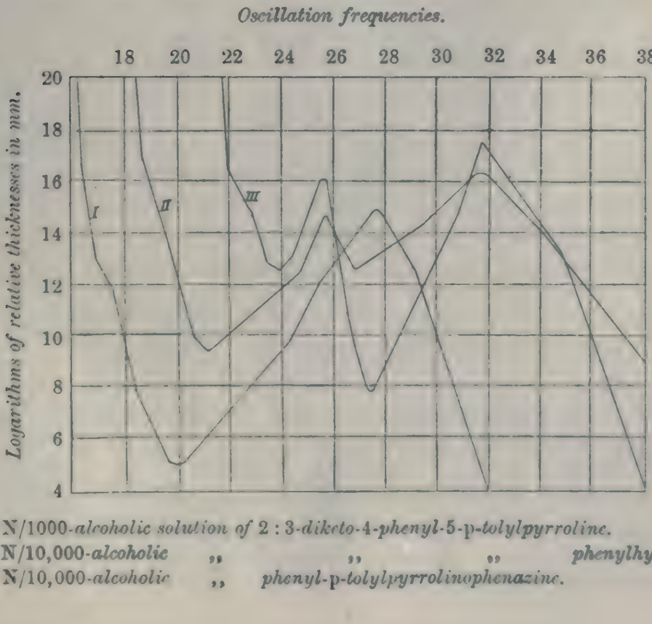
To sum up these observations, it is clear (1) that the diketonic structure means the production of a dark red colour, and a corresponding well-marked absorption band, the position of which differs slightly, corresponding with differences in the dark red shade; (2) the introduction of a methyl or

FIG. 3.



I. N/1000-*alcoholic solution of diketodiphenylpyrroline.*
II. N/10,000-*alcoholic* ,, *diketodiphenylpyrrolinephenylhydrazone.*
III. N/10,000-*alcoholic* ,, *diphenylpyrrolinophenazine.*

FIG. 4.



I. N/1000-*alcoholic solution of* 2 : 3-*diketo*-4-*phenyl*-5-p-*tolylpyrroline.*
II. N/10,000-*alcoholic* ,, ,, ,, *phenylhydrazone.*
III. N/10,000-*alcoholic* ,, *phenyl*-p-*tolylpyrrolinophenazine.*

a propyl group in an aromatic side-chain produces no fundamental change either in the colour or in the absorption band; (3) if either a methoxy- or a methylenedioxy-group is introduced in an aromatic side-chain, the deep red colour and corresponding band are still retained, but another more refrangible band is produced characteristic of the type of the introduced radicle; (4) when one of the oxygen atoms of the diketonic groups is replaced by the $:N\cdot NHPh$ group, the colour is changed from dark red to carmine-red; the corresponding less refrangible absorption band is reduced in intensity and its position is shifted towards the more refrangible side; and another weaker band is produced beyond this on the more refrangible side; (5) the replacement of both oxygen atoms of the diketonic groups, and the production of the phenazine ring $\begin{matrix}:N\\:N\end{matrix}>C_6H_4$, changes the colour from carmine-red to lemon-yellow, and the corresponding band is also shifted towards the more refrangible end. This band is also less intense, and the second more refrangible band becomes much stronger; and (6) corresponding with these changes in colour and selective absorption, the positions of general absorption are shifted towards the more refrangible region of the spectrum.

The observations, then, indicate that the absorption is intimately connected with the presence of a diketonic grouping. Baly and Stewart (Trans., 1906, **89**, 502) have suggested that the residual affinities of the dicarbonyl compounds studied by them are oscillating between two extreme phases. But in these compounds it may be equally valid to say that the maximum valencies of the oxygen atoms come into action, resulting in the production of a closed ring produced by the two oxygen atoms, and the consequent production of absorption. On this suggestion the ring is destroyed by the elimination of the oxygen in the hydrazone linking; the intensity of the original band is lessened, and another band is produced, accompanied by changes in the colour and absorption in the visible spectrum from the less to the more refrangible regions. The further production of the phenazine ring does not wholly destroy the original absorption; it simply decreases it, and another band is produced characteristic of the new type of ring.

From these considerations, it seems to be difficult to resist the conclusion that the original band, which corresponds with the deep red colour, is caused by the oscillation or vibration of the original diketopyrroline ring, and that it is modified by the elimination of the ketonic groups. In connexion herewith, it should be mentioned that the author found no bands in phenylhydrazine in solutions of $N/10$-, $N/100$-, $N/1000$-, and $N/10{,}000$-strengths through varying thicknesses of 2 mm. to 30 mm. Also, Hartley and Dobbie (Trans., 1898, **73**, 598) found no bands in alcoholic solutions of pyrrole, and this has been confirmed by the author (this vol., p. 1648).

I have again to thank the Government Grant Committee of the Royal Society, by whose assistance the spectroscope used in this research was obtained, and also Dr. Ruhemann for specimens of the pure substances.

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CCLX.—*Researches on Bleaching Powder.*

By ROBERT LLEWELLYN TAYLOR.

FOR the purpose of this investigation, it was first of all necessary to devise a method for distinguishing between pure chlorine and hypochlorous acid, and, in a mixture of the two, finding their proportions.

The method used was to pass the gases through a known volume of *N*/10-sodium arsenite. The action of chlorine and of hypochlorous acid on sodium arsenite may be represented thus:

$$(1)\ As_2O_3 + 2Cl_2 + 2H_2O = As_2O_5 + 4HCl.$$

$$(2)\ As_2O_3 + 2HOCl = As_2O_5 + 2HCl.$$

It is plain that, for the same amount of arsenite oxidised, twice as much hydrochloric acid (or chloride) is produced in the case of chlorine as in the case of hypochlorous acid. The arsenite (which must always be in excess, so that it is not completely oxidised) is then divided into two equal parts. In one-half, the amount of arsenite remaining unoxidised is determined by means of *N*/10-iodine solution, and from this the amount oxidised is ascertained. In the other half, the amount of chlorine is determined by means of *N*/10-silver nitrate. In the latter determination the use of an indicator was very soon discarded, although, if a considerable proportion of the arsenite has been oxidised, the arsenate produced acts fairly well as an indicator, and may be used instead of adding a chromate to the solution. Much more trustworthy results, however, are obtained by acidifying the solution with nitric acid, adding a little of the silver solution, boiling for a minute or two, and then filtering a portion of the liquid. A little more of the silver solution is added, drop by drop, to the filtered portion, which is then returned to the bulk, and this boiled and filtered again. This is continued until the filtered portion gives no further precipitate with the silver solution. As described, the process seems tedious, but in practice it works very well, and the determination of the chlorine can be made fairly rapidly. In this process, as the solutions used are all decinormal, and therefore equal to each other, when the oxidising agent is pure chlorine, the amount of silver nitrate used (=amount of chloride present) is the same as the amount of arsenite oxidised. When hypochlorous acid is the oxidising agent, the chloride produced is only half the amount of arsenite oxidised.

The Action of Carbon Dioxide on Bleaching Powder.

It is very frequently stated, and probably usually considered, that carbon dioxide simply liberates hypochlorous acid from bleaching powder. A considerable number of observers, however, have pointed out that chlorine is produced when pure carbon dioxide acts on bleaching powder.

Thus, Richards and Juncker (*Dingl. Polyt. J.*, 1874, **211**, 31) state that dry bleaching powder is almost undecomposed by carbon dioxide. If about 10 per cent. of water is present, both chlorine and hypochlorous acid are produced.

Wolters (*J. pr. Chem.*, 1874, [ii], **10**, 128) refers to the liberation of chlorine by the action of carbon dioxide on bleaching powder, and Lunge and Schäppi (*Dingl. Polyt. J.*, 1889, **273**, 63) state that carbon dioxide expels nearly the whole of the chlorine from bleaching powder.

Dreyfus (*Bull. Soc. chim.*, 1884, [ii], **41**, 600) found that carbon dioxide has no action on calcium chloride, but, in the presence of chlorine monoxide, either dry or in aqueous solution, it liberates chlorine.

More recently this question, with others relating to bleaching powder, has been investigated by von Tiesenholt (*J. pr. Chem.*, 1901, [ii], **63**, 30; 1902, [ii], 512; 1906, [ii], **73**, 301). Some of his conclusions will be referred to later.

In my first experiments, carbon dioxide, in its ordinary moist condition, after being well washed with water, was passed through a U-tube containing bleaching powder and a sufficient amount of glass wool to give a free passage for the gas. Carbon dioxide, as ordinarily prepared by the action of hydrochloric acid on marble, invariably carries with it a little hydrochloric acid, and, in some of the experiments, this was removed by passing the gas through glass wool wetted with a solution of silver nitrate, which acts quite effectually. When, however, the gas is well washed with water, the amount of hydrochloric acid accompanying it is not sufficient seriously to affect the results. After passing through the bleaching powder, the gas was passed through a Bunsen U-tube containing *N*/10-sodium arsenite.

A considerable number of experiments were made, and the following is an example of the results invariably obtained. Twenty c.c. of the *N*/10-arsenite were used:

I.

Amount of arsenite oxidised	8·35 c.c.
Amount of *N*/10-silver nitrate used	8·4 c.c.

It is plain from this that the sole product of the action of carbon dioxide on bleaching powder is chlorine. The escaping gas has a strong odour of chlorine, and none at all of hypochlorous acid. The action proceeds very rapidly if the carbon dioxide is quite moist.

In some further experiments, the carbon dioxide was dried by passing it over calcium chloride. The effect of drying the gas is that the action becomes much slower, and, as the moisture usually present in the bleaching powder is gradually carried away by the dry carbon dioxide, it soon becomes extremely slow. When this point has been reached, the instantaneous acceleration of the action when the drying tube is removed is very striking. The following three experiments show that the product is the same with the dry as with the moist gas, namely, nothing but chlorine:

II.

	Arsenite oxidised.	Chloride produced.
1.	3·4	3·5
2.	1·9	1·95
3.	6·55	6·65

The slight excess of silver nitrate used may have been due to a little hydrochloric acid carried over, although the actual amounts are not beyond the limits of accuracy of the method.

When carbon dioxide is passed through a solution of bleaching powder in water, the action is very rapid, but the result is exactly the same, as the following experiments show:

III.

	Arsenite oxidised.	Chloride produced.
1.	5·6	5·58
2.	3·1	3·1

The issuing gas again had a strong odour of chlorine, and none at all of hypochlorous acid.

Action of Carbon Dioxide on a Mixture of Sodium Chloride and Hypochlorite, and on a Mixture of Bromide and Hypobromite.

The mixture of sodium chloride and hypochlorite was prepared by passing chlorine into a moderately concentrated cold solution of sodium hydroxide. The following experiments show that the action is exactly the same as with a solution of bleaching powder:

IV.

	Arsenite oxidised.	Chloride produced.
1.	4·1	4·12
2.	6·1	6·13

When carbon dioxide is passed through a solution containing a mixture of a bromide and a hypobromite there is, as one would naturally expect, an immediate and copious liberation of bromine.

It is well known that carbon dioxide acts in a similar way on a mixture of iodide and hypoiodite.

It appears, from the foregoing experiments, that the action of carbonic acid on bleaching powder and similar substances is exactly like that of any other acid. There has been much discussion as to the actual constitution of dry bleaching powder, but, whatever that constitution may be, it may be taken that, in solution or in presence of water, it is, to all intents and purposes, a mixture of chloride and hypochlorite. The usual explanation of the action of, say, sulphuric acid (when used in considerable quantity) on bleaching powder is that the chloride and hypochlorite are both decomposed, with the simultaneous production of hydrochloric and hypochlorous acids, and that these decompose each other, with the liberation of chlorine. The question is whether or not we must seek for some other explanation of the action of carbonic acid. There would seem to be no doubt that the action of carbonic acid is exactly like that of other acids. Of course, this involves the conclusion that calcium chloride (or sodium chloride, for example) is decomposed, when in solution, by carbonic acid, with the liberation of hydrochloric acid, and that, therefore, the action of hydrochloric acid on carbonates is a reversible one:

$$CaCO_3 + 2HCl \rightleftharpoons CaCl_2 + H_2CO_3.$$

I have tried to obtain some experimental evidence that this is the case, and not altogether without success.

Many years ago Müller (*Journ. Chem. Soc.*, 1870, **23**, 36) stated that a solution of lead chloride is decomposed when carbon dioxide is passed through it, with liberation of hydrochloric acid and precipitation of a chlorocarbonate, and that some of the liberated acid could actually be distilled off. He also stated that carbon dioxide, under considerable pressure, would decompose sodium and calcium chlorides, when in solution in water, with liberation of hydrochloric acid. He used ultramarine as an indicator, and stated that, whilst carbon dioxide alone does not decompose ultramarine suspended in water, even under considerable pressure, if the water contains common salt dissolved in it the colour of the ultramarine is destroyed.

I am unable to confirm the latter observation. Carbon dioxide, when bubbled through water in which a little ultramarine is suspended, has no effect on it, whether the water contains salt or not. Under a pressure of a few atmospheres, however, ultramarine is decomposed and decolorised by carbonic acid alone, and I have been unable to observe any difference in the action when the water contained salt as well. The experiments I made were performed in an ordinary sparklet apparatus, in which the pressure attains five or six atmospheres. If distilled water with a little ultramarine suspended in it is placed in such an apparatus, and then the liquid charged with carbon dioxide in the usual way, there is no immediate effect, but, in the course of a day or two, the colour of the ultramarine gradually disappears. As stated above, the presence of salt (or of calcium chloride) in the water makes no apparent difference in the result.

Methyl-orange is, however, a much more delicate indicator for acids than ultramarine. It is usually assumed that the former is not affected by carbonic acid, but this is not quite correct. If well washed carbon dioxide is bubbled through distilled water containing a little methyl-orange, there is a distinct alteration of the colour, although it does not turn pink. If, however, the water contains also a little pure salt, or calcium chloride, or potassium chloride, the colour becomes distinctly pink when the carbon dioxide is bubbled through. The change of colour is most striking in the case of the common salt, but it is quite evident with the other chlorides. This may be taken as evidence that carbonic acid liberates a sensible amount of hydrochloric acid in solutions of chlorides, that is to say, the action of hydrochloric acid on carbonates is a reversible one. Of course, the amount of hydrochloric acid thus liberated must be extremely small, but it will be quite sufficient to explain the action of carbonic acid on bleaching powder and similar substances. The small amount of hydrochloric acid liberated will be at once decomposed by the hypochlorous acid liberated simultaneously from the hypochlorite; this will enable the action of the carbonic acid to proceed as before, and so there will be a continuous evolution of chlorine, and, if this is carried away as fast as it is formed, the bleaching powder will be almost completely decomposed.

It may here be noted that if carbon dioxide is bubbled through water containing potassium bromide or ammonium chloride and coloured with methyl-orange, the change of colour is not so striking as in the case of the three chlorides mentioned above. Pure water coloured with methyl-orange becomes quite pink when charged with carbon dioxide in a sparklet apparatus.

Von Tiesenholt (*loc. cit.*) explains the production of chlorine when carbon dioxide acts on bleaching powder by supposing that hypochlorous acid is first formed by the action of the carbon dioxide on the hypochlorite present, and that this acts on the calcium chloride, liberating chlorine:

$$CaCl_2 + 2HOCl = Ca(OH)_2 + 2Cl_2.$$

He finds, in confirmation of this view, that chlorine is liberated when a solution of hypochlorous acid is added to calcium chloride or to common salt. The experiments here described, however, show that nothing but chlorine is produced by the action of carbonic acid on bleaching powder, so that all the hypochlorous acid which is liberated must be decomposed. Apparently, if von Tiesenholt's view is right, hypochlorous acid cannot exist in the presence of a sufficient amount of a chloride, so that it would be impossible to expel any hypochlorous acid from a solution which contains chlorides. As will be seen later, however, mixtures of chlorine and hypochlorous acid containing a considerable proportion of the latter can be expelled from solutions of bleaching powder. Consequently, whilst it is possible that the action of hypochlorous acid on chlorides may account for some of the chlorine which is produced in the case of concentrated solutions or the merely moist bleaching powder for example, von Tiesenholt's explanation would not appear to be preferable to the one offered above.

The Action of Air on Bleaching Powder.

Although this was not the order in which the experiments were actually tried, it will be best to describe first the effect of air from which all the carbon dioxide has been removed. This was done by passing the air through washing cylinders containing coke wet with a concentrated solution of sodium hydroxide. It was then bubbled through a milky solution of bleaching powder (about 5 to 10 per cent.), and afterwards through the solution of sodium arsenite.

In all the experiments with air, it was passed through at a rate of about 10 to 15 litres per hour.

Air free from carbon dioxide is practically inert so far as bleaching powder is concerned, and naturally all that it can do is to sweep out any chlorine or hypochlorous acid which may happen to be present. Consequently, the action is very slow, and the experiments had to be carried on for a long time (from seventy-two to ninety-six hours) in order to obtain sufficient oxidising action in the solution of arsenite to be able to judge what was being carried over. The following results were obtained in three separate experiments:

V.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1.	1·08	0·57	90	10
2.	1·0	0·45	100	0
3.	0·8	0·38	100	0

The amount of oxidation in these experiments was very little, but they appear to show that a small amount of free hypochlorous acid exists in a solution of bleaching powder, which is simply swept out by the passage of air free from carbon dioxide through it. Probably the free hypochlorous acid is due to the calcium hypochlorite in a dilute solution being slightly hydrolysed, thus:

$$Ca(OCl)_2 + 2H_2O \rightleftharpoons Ca(OH)_2 + 2HOCl.$$

This possibly accounts for the fact that solutions of bleaching powder have an odour of hypochlorous acid.

One similar experiment to the above was made in which the solution of bleaching powder was kept at a temperature of about 40° the whole of the time. In this experiment, also, practically nothing but hypochlorous acid was swept out, the only difference being that, as one would expect, the time required was rather less.

Action of Ordinary Air on Bleaching Powder.

A considerable number of experiments were made with ordinary air, passing it through a tube containing dry bleaching powder, and then through the solution of arsenite. At first the action is rather slow, but, as the bleaching powder gradually becomes wet, the action proceeds more and more rapidly. In some of the experiments the moisture of the air was purposely increased by passing it through a tube containing wet glass wool. In each of the two following series of experiments the same tube of bleaching powder was used throughout. The time occupied by each experiment varied from about twenty-four hours at the beginning to six hours when the bleaching powder had become wet:

VI.

Series 1.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1.	4·45	4·0	11	89
2.	2·9	2·56	13	87
3.	2·55	2·3	10	90
4.	7·0	6·95	0	100
5.	7·9	7·95	0	100

Series 2.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1.	2·1	1·83	15	85
2.	3·35	3·1	8	92
3.	6·0	6·05	0	100

The above experiments are selected from a considerable number, and they all tend to show that, at the outset, ordinary air sweeps out from bleaching powder a mixture containing from 80 to 90 per cent. of chlorine, and from 10 to 20 per cent. of hypochlorous acid, but that, as the action proceeds, the amount of hypochlorous acid gradually diminishes, and at last nothing but chlorine appears. The gradation of the experiments is not the same in the two series, but that is partly due to the fact that some intermediate experiments in both series were spoiled by going on too long.

When ordinary air is passed through a solution of bleaching powder (not filtered, and containing about 5 to 10 per cent. of the powder), the proportion of hypochlorous acid swept out is considerably greater, as indeed one would expect if we accept the suggestion that the hypochlorous acid is due to hydrolysis of the calcium hypochlorite. As in the case of the dry powder, however, the amount of hypochlorous acid gradually diminishes as the experiment proceeds, although it does not disappear altogether. The following experiments were made with the same solution of bleaching powder, in the order in which they are given. In experiment No. 4, the proportion of hypochlorous acid appears to have risen slightly, but the method of determining it is not accurate enough to enable one to say that the amounts in experiments 3 and 4 were not substantially the same. The action was very slow in the first experiment, but much more rapid afterwards:

VII.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1.	4·48	2·94	52	48
2.	9·15	7·27	25	75
3.	3·18	2·88	10	90
4.	3·34	2·87	16	84

It must be pointed out that the above numbers, showing the relative amounts of hypochlorous acid and chlorine swept out of the liquid by the air, do not necessarily represent the actual proportions present at any moment in the liquid itself. There is no doubt that chlorine, being less soluble in water than hypochlorous acid, will be swept out more readily, so that the proportion of hypochlorous acid actually present in the liquid is certainly greater than the above numbers indicate.

These results, showing the action of ordinary air on bleaching powder, are very remarkable. The difference between the action of ordinary air and air from which the carbon dioxide has been removed is, at first sight, almost incredible. Whereas the latter simply sweeps out from a solution of bleaching powder (although very slowly) practically pure hypochlorous acid, the presence of the really very small amount of carbon dioxide which usually exists in ordinary air causes the action to proceed much more rapidly (although not with anything like the rapidity with which pure carbon dioxide acts), and, after a time, has almost the same effect, so far as the product is concerned, as passing pure carbon dioxide through it.

I have already expressed the opinion that the action of pure moist carbon dioxide on bleaching powder is the same as that of other acids—it is a mass action, and the carbonic acid decomposes both the chloride and the hypochlorite. Whilst one may accept this explanation in the case of pure carbon dioxide used in comparatively large quantities, and always locally in large excess, it is impossible to believe that the small amount of carbon dioxide present in ordinary air can act in the same way. We must therefore look for some other explanation.

The Action of Chlorine on Alkalis a Reversible Action.

In former papers (*Mem. Manchester Phil. Soc.*, 1897, **41**, No. VIII; Trans., 1900, **77**, 725) I have pointed out that the action of iodine on alkalis is a reversible one. If an alkali is added to a solution of iodine in water or in potassium iodide until the colour just disappears, the addition of potassium iodide to the solution causes the liberation of some of the iodine:

$$2KOH + I_2 \rightleftharpoons KI + KOI + H_2O.$$

The addition of the extra amount of potassium iodide causes the reaction to proceed from right to left in the above expression. Also, and this, too, follows from the fact that the action is reversible, the amount of alkali needed to complete the reaction from left to right and to remove the colour of the iodine is considerably more than is required by the equation, so that the almost colourless solution of iodide and hypoiodite always contains some free alkali.

When these experiments were made, similar ones were also performed with bromine and alkalis, but analogous results were not obtained. The reason of this must have been that too strong a solution of bromine was used, because I find that the reversibility of the action of bromine on alkalis is quite as striking as that of iodine if a very dilute solution of bromine is employed. The action is not nearly so easy to see with ordinary bromine water, but if this is diluted with ten to twenty times its bulk of water, and then sodium or potassium hydroxide added drop by drop until the colour of the bromine has disappeared, the addition of a little concentrated solution of potassium bromide causes a manifest liberation of bromine. The liberation of bromine is seen still more plainly if, instead of the solution of potassium bromide, a considerable amount of the powdered salt is added. The addition of the extra potassium bromide causes the action to proceed from right to left:

$$2KOH + Br_2 \rightleftarrows KBr + KOBr + H_2O.$$

It is perfectly reasonable to suppose, then, that the action of chlorine on alkalis is also a reversible action. This has already been suggested by von Tiesenholt (*loc. cit.*), who describes a number of experiments which point to this conclusion. I have been able to demonstrate, by experiments which are described later, that this conclusion is correct, and it will be seen that it supplies a perfectly satisfactory explanation of the action of ordinary air on bleaching powder, and that it also explains some well-known facts with regard to some bleaching solutions which have been hitherto apparently inexplicable.

If we represent the action of chlorine on sodium hydroxide and on slaked lime thus:

$$2NaOH + Cl_2 \rightleftarrows NaCl + NaOCl + H_2O$$

and

$$2Ca(OH)_2 + 2Cl_2 \rightleftarrows CaCl_2 + Ca(OCl)_2 + 2H_2O.*$$

it is plain that the chlorides produced by the action are continually tending to reverse the reaction, so that, to carry it to a finish from left to right, there must always be a considerable amount of free sodium hydroxide or lime present. It is a well-known fact that bleaching powder always contains a considerable amount of free lime, and that it is impossible to prepare it otherwise. If this free lime, or a portion of it, is removed, then the reaction will proceed in the opposite direction to a greater or less extent, and chlorine will be liberated.

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* It is not suggested that this equation represents what actually occurs in the manufacture of bleaching powder, but simply the condition of equilibrium in which it exists when wet or in solution.

A number of experiments were made to test this point. A filtered solution of bleaching powder was employed, having a specific gravity of 1·03 to 1·06 in different experiments. In order to remove some of the free lime, the solution was exposed to air for some hours in a shallow dish, with occasional shaking. The amount of free lime present in such a solution is considerable, and the latter becomes very milky on exposure to air. The liquid was filtered from the precipitated calcium carbonate, and air free from carbon dioxide was passed through it and into the arsenite solution in the usual way. The following are some of the results obtained:

VIII.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1.	4·0	3·16	26	74
2.	3·8	3·0	27	73
3.	2·6	1·8	44	56
4.	5·92	5·15	15	85
5.	4·35	4·04	8	92
6.	2·27	1·52	50	50

Most of the separate experiments were made with different portions of the solution, which had been exposed to air for different lengths of time, so that the extent to which the free lime was removed varied. Doubtless this accounts for the irregularity in the results. In all the above experiments the action was much more rapid than was the case with the solution from which none of the free lime had been removed, the rapidity evidently depending on the extent to which this removal had been carried. It will be noted that besides the large quantities of free chlorine produced, in most of the experiments the amount of hypochlorous acid swept out from the liquid was very much greater than was the case with the solution from which no free lime had been removed. This is quite what one would expect to occur. The hypochlorous acid, as before stated, is probably due to hydrolysis of the calcium hypochlorite in the solution. This also is a reversible action, and as one of the products of the hydrolysis is free lime, the removal of the lime naturally stimulates this action as well.

These experiments demonstrate quite sufficiently the reversibility of the reaction betwen chlorine and calcium hydroxide. As the free lime is more or less removed, the reaction proceeds in the opposite direction, and chlorine is liberated. In these experiments the free chlorine is swept out of the solution, but it is continually being reproduced, the steady removal of the chlorine allowing the reverse action to take place continuously. If the free chlorine were removed from the solution in any other way, by bleaching, for example, it would in the same way be continually reproduced as long as any of the bleaching substance remained. It follows from this, of course, that the bleaching action of a solution of bleaching powder will be stimulated by the removal of free lime from the solution. This will be referred to again later.

The action of ordinary moist air on bleaching powder, both solid and in solution, described on p. 2548, is now perfectly intelligible. The carbon dioxide in the air combines with the free lime, and, as this gradually diminishes and finally practically disappears, the reverse action proceeds freely, and, of course, chlorine is produced.*

It is usually understood, and has been frequently stated, that a pure solution of hypochlorous acid bleaches more energetically and more rapidly than free chlorine. It may be doubted whether this is really the case. I have prepared practically pure solutions of hypochlorous acid, and compared its action with that of a solution of chlorine on various colouring matters, and I have failed to find any evidence of the greater activity of hypochlorous acid. Rather the contrary. With a solution of indigo-carmine, for example, the bleaching action of chlorine is much more rapid than that of hypochlorous acid—in the case of the latter the action is to be described as sluggish, rather than rapid. This is an important point, because I am strongly of opinion that in the use of solutions of bleaching powder and similar substances for bleaching purposes, most of the actions generally attributed to hypochlorous acid are really due to chlorine, and that, in practice, hypochlorous acid plays only a minor part in bleaching.

It is remarkable how the bleaching action of a solution of bleaching powder is stimulated by the mere removal of the free lime in it. If a strip of Turkey-red calico is placed in a clear solution of bleaching powder so that it is completely immersed in the liquid, and if the liquid is kept in a closed vessel so that air has no access to it, there is scarcely any bleaching action at all, even after several days. If, however, the solution is placed in a basin or a shallow dish, so that air has free access, and if a small portion of the red calico is left outside the liquid, so that it is reached by the solution and the air at the same time, the portion outside is bleached quite rapidly. Further, if the coloured calico is completely immersed in a little of the solution contained, say, in a deep test-tube, and the test-tube is breathed into about half a dozen times, shaking after each time, the calico is very soon bleached. Also, whilst, as stated above, a fresh solution of bleaching powder has very little, if any, bleaching action on a piece of red calico completely immersed in it, if the solution has been exposed to air in a shallow dish for a few hours, with occasional shaking, then a piece of red calico completely immersed in it is bleached rapidly.

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* It may be asked if the removal of free lime by carbon dioxide is a satisfactory explanation of the fact that ordinary air expels chlorine from bleaching powder, would not this also explain the action of pure carbon dioxide on bleaching powder, so that there would be no need to assume, as is done in the first part of this paper, that carbonic acid decomposes chlorides with the liberation of hydrochloric acid? The author adheres to the latter explanation simply because the action of carbon dioxide is so much more rapid than that of air. A stream of carbon dioxide through a solution of bleaching powder liberates chlorine from ten to twenty times more rapidly than air at its quickest, and the action altogether suggests a rapid and complete decomposition, such as is effected by other acids, rather than the mere sweeping out of chlorine produced by the reversed action.

A simple but very striking experiment which illustrates the same point is to immerse a strip of ordinary red litmus paper in a fresh solution of bleaching powder. The paper is turned blue, and in a short time it is bleached. If, however, immediately after it has been dipped in the solution, it is breathed upon, it is bleached almost instantly. A solution of bleaching powder which has been well exposed to air, as described above, bleaches litmus paper at once.

In all these cases the more rapid bleaching action is simply due to the removal of free lime, and I think it is plain, also, if reference is made to the experiments, series VIII, on p. 2551, that the principal bleaching agent is chlorine, and not hypochlorous acid. Certainly those experiments show that in some cases a considerable proportion of hypochlorous acid is swept out, but in all cases the rapidity of the bleaching action is roughly proportional to the extent to which the free lime is removed, and the more completely that is done the greater is the proportion of chlorine liberated.

It is a fact, well known in bleach-works, that an old vat is more active than a new one. The reason for this is obvious. Exposure to air, especially if the liquid is frequently stirred, gradually causes the removal of the free lime.

If the action of chlorine on lime is, as I think the above experiments sufficiently demonstrate, a reversible action, then the reverse action must be stimulated by the addition of calcium chloride to the solution. Experiments were made to see if this is the case. After experiment No. 2 (series VIII) on p. 2551 was finished, a considerable amount of crystallised calcium chloride was added to the same solution of bleaching powder and air free from carbon dioxide passed through it again. The action became considerably more rapid, and the effect of the calcium chloride is seen by a comparison of the two experiments. No. 1 was before, No. 2 after, the addition of the calcium chloride.

IX.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1.	3·8	3·0	27	73
2.	4·75	4·73	0	100

The solution used in experiment No. 6 (series VIII) was treated in the same way with the following result:

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1.	2·27	1·52	50	50
2.	5·4	4·92	10	90

These experiments show plainly that, as anticipated, the reverse action is greatly increased by the addition of more calcium chloride.

Other chlorides, of course, ought to have a similar effect. The following experiments show the effect of adding common salt to the solution. As before, the greater part of the free lime in the solution was removed by exposing it to air. Experiments 1 and 2 were successive experiments before the addition of the salt, and No. 3 shows the effect of the salt. The salt was added in considerable quantity—almost sufficient to saturate the solution.

X.

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1.	1·75	1·4	25	75
2.	5·25	4·1	28	72
3.	6·53	6·55	0	100*

The addition of the salt in the above experiment caused the action to proceed much more rapidly. Thus, whilst in experiment No. 2 it took twenty hours to oxidise 5·25 c.c. of the arsenite solution, in experiment No. 3, 6·53 c.c. were oxidised in four hours, the carbon dioxide-free air passing through at approximately the same rate in both experiments.

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* The apparently complete disappearance of hypochlorous acid indicated in experiments 2 (IX) and 3 (X) is very remarkable, and seems difficult to explain. It is not claimed, however, that the method used for determining the relative amounts of chlorine and hypochlorous acid is perfectly accurate. It is doubtful whether it would be possible to determine very small proportions of hypochlorous acid by it. It must also be borne in mind (see p. 2549) that chlorine is more easily swept out from the solution than hypochlorous acid, so that it is possible that the latter does not altogether disappear. Possibly, also, von Tiesenholt's explanation (see p. 2546) may apply here, and the hypochlorous acid may be all decomposed by the large quantities of chlorides present in the solution.

Experiments were also made to see the effect of the addition of calcium chloride and salt to an ordinary solution of bleaching powder, without removing any of the free lime. The free lime in the solution, of course, tends to stop the reverse action, so that the effect of adding calcium chloride or salt to the solution is not nearly so great as when the free lime is first removed. The following is the result of the two experiments tried.

To No. 1 calcium chloride was added, and to No. 2 common salt —both in large quantity. The action proceeded very slowly indeed in both experiments, but the results are sufficient to show that, even in ordinary bleaching powder solution, the addition of chlorides has a sensible effect in reversing the action:

	Arsenite oxidised.	Chloride produced.	Hypochlorous acid, per cent.	Chlorine, per cent.
1.	2·24	2·22	0	100
2.	2·66	2·4	10	90

It follows from the above experiments that the addition of calcium chloride or salt to a solution of bleaching powder must exercise a stimulating effect on the bleaching action of the solution. This is actually the case. If some of the free lime has been removed from the solution, the effect of the addition of considerable amounts of calcium chloride or salt on the bleaching action is very striking. With bleaching powder solution in its ordinary state, containing the usual amount of free lime, the effect on its bleaching action of adding calcium chloride or salt is, for the reason pointed out above, not nearly so great, although it is quite sufficiently marked.

I understand that it has been found, in actual bleaching, that the addition of either calcium chloride or salt stimulates the action, but I am not aware that any satisfactory explanation of this stimulating effect has hitherto been given. It may perhaps be worth the while of practical bleachers to note that the addition of calcium chloride or salt has a much greater effect when some of the free lime has been removed—by exposing the solution to air, for example.

Bleaching solutions made by the electrolysis of a solution of salt have latterly come into considerable use, and I understand that the fact has been frequently noted that a solution of sodium hypochlorite thus prepared is more active than a solution of sodium hypochlorite, containing the same proportion of available chlorine, prepared by the addition of sodium carbonate to a solution of bleaching powder and allowing the precipitated calcium carbonate to settle. The explanation of this is obvious when it is understood that, in preparing the electrolytic bleaching solution, only a small fraction of the salt in the solution is usually decomposed. The solution thus differs from that made by the other method by containing a large amount of salt, and the effect of this is to increase the reverse action and so to liberate chlorine in the solution. Also, in the electrolysis of the salt, chlorine and sodium hydroxide are produced in exactly equivalent proportions, so that there cannot be a sufficient amount of the latter to absorb the whole of the chlorine. Under these conditions, the reversing action of the excess of salt will naturally be very considerable. The greater bleaching activity of such a solution is therefore perfectly natural, and exactly what one would expect.

In addition to the experiments described in this paper, I have used my method for distinguishing betwen hypochlorous acid and free chlorine for investigating the action of various acids on bleaching powder and similar substances. This investigation is still proceeding.

Summary.

1. The action of carbon dioxide on bleaching powder and similar substances results in the liberation of chlorine only—no hypochlorous acid. The conclusion is drawn that the action is like that of any other acid, and that carbonic acid decomposes both the chloride and the hypochlorite in the bleaching powder. It follows from this that the action of hydrochloric acid on carbonates is a reversible one.

2. Ordinary moist air acts on solid bleaching powder, liberating at first both chlorine and hypochlorous acid, the former in much the larger amount. After a time nothing but chlorine is produced. When ordinary air is passed through a solution of bleaching powder, a mixture of hypochlorous acid and chlorine is swept out, at first in about equal amounts; but, as the experiment proceeds, the former diminishes, and the latter increases to about 90 per cent.

3. The action of chlorine on alkalis, like that of iodine and bromine, is a reversible one, as stated by von Tiesenholt. If the free lime in bleaching powder is removed, this causes the reverse action to proceed, and thus chlorine is liberated. This explains the action of ordinary air on bleaching powder. The reversibility of the action also explains the stimulating effect on bleaching which the addition of calcium chloride or of salt causes in a solution of bleaching powder.

4. In the ordinary processes of bleaching the active bleaching agent is probably free chlorine, hypochlorous acid playing only a minor part.

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CCLXI.—*The Colour and Constitution of Diazonium Salts. Part III. The Diazo-derivatives of* 2 : 7-*Naphthylenediamine.*

By Gilbert T. Morgan and Frances M. G. Micklethwait.

Although the diazo-derivatives of the diamines of the benzene and diphenyl series have been extensively studied, owing largely to the circumstance that in many instances these products are of considerable industrial importance, yet comparatively little attention has been directed to the diazonium salts of the naphthylenediamines. Of the ten naphthylenediamines, three, namely, the 1 : 2-, 2 : 3-, and 1 : 8-compounds, are known to yield cyclic diazoimines (De Aguiar, *Ber.*, 1874, **7**, 316; Friedländer and von Zakrzewski, *Ber.*, 1894, **27**, 764; Morgan and Godden, this vol., p. 1707); the remaining seven give diazonium salts of varying degrees of stability (Ewer and Pick, D.R.-P. 45549, 45788; Badische Anilin- & Soda-Fabrik, D.R.-P. 130475).

The case of 2 : 7-naphthylenediamine has recently been examined by Kaufler in connexion with his theory of the stereochemical configuration of naphthalene and other polynuclear hydrocarbons. According to Kaufler, the two nuclei present in naphthalene are bent round, using their two common carbon atoms as axis, so that the lateral extremities of the molecule represented by the positions 2 : 3 and 6 : 7 become contiguous. This supposed folding of the two nuclei would bring the two amino-groups of 2 : 7-naphthylenediamine into close proximity, and Kaufler claims that the intimate association of these two groups is manifested by certain phenomena of steric hindrance which are advanced in support of his hypothesis * (*Annalen*, 1907, **351**, 154; *Ber.*, 1907, **40**, 3251).

It is asserted that the amino-groups of 2 : 7-naphthylenediamine exert a mutual inhibiting influence on each other, with the result that only one amino-group is diazotisable. In diazotising the hydrobromide or the hydrochloride of the diamine, Kaufler and Karrer worked in acetic acid or alcoholic solution, and found that even with excess of amyl nitrite only the monodiazonium salt was precipitated (*Ber.*, 1907, **40**, 3263).

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* It may be pointed out that Kaufler's view is at variance with the ideas embodied in the Kekulé-Baeyer conception of the naphthalene molecule based on the tetrahedral carbon atom and the strain hypothesis, and also with the naphthalene model advocated by Pope and Barlow on crystallographic grounds. These conceptions, which may be termed respectively the functional and structural representations of naphthalene, although differing in many respects, concur in placing the 2 : 3- and 6 : 7-positions, not in contiguity, but at the lateral extremities of the molecule.

This result is dependent, however, not on steric hindrance, but on experimental conditions. By operating with sodium nitrite or nitrosyl sulphate in moderately concentrated sulphuric acid, the authors have succeeded in diazotising completely both the amino-groups of the diamine. Probably the diazotisation occurs in two stages, and the isolation of the intermediate amino-diazonium salts by Kaufler and Karrer is dependent on the insolubility of these substances in the media employed.

EXPERIMENTAL.

*Naphthalene-*2 : 7-*bisdiazonium Sulphate* (I), $HSO_4\cdot N_2\cdot C_{10}H_6\cdot N_2\cdot HSO_4,\frac{1}{2}C_2H_5OH$.

Recrystallised 2 : 7-naphthylenediamine (0·5 gram), melting at 160—161°, was dissolved in 2 c.c. of cold concentrated sulphuric acid, mixed with 1 gram of ice, and diazotised with 2 grams of nitrosyl sulphate, the mixture being cooled by further addition of 1 gram of ice. The cold filtered solution was carefully added to a mixture of two parts of ether and one of alcohol, and if the precipitated sulphate was viscid, more alcohol was added. The light yellow crystals thus obtained were washed with a mixture of ether and alcohol, and finally with ether; the yield of diazonium sulphate was 86 per cent. of the calculated quantity. The salt was appreciably soluble in alcohol, and when precipitated by ether in the presence of alcohol it retained a definite amount of the latter solvent, even after prolonged drying in the vacuum desiccator. The following analyses were carried out on different preparations which had been dried for varying periods:

0·2116 gave 0·2562 CO_2 and 0·0562 H_2O. C = 33·02; H = 2·95.
0·1385 „ 0·1688 CO_2 „ 0·0334 H_2O. C = 33·24; H = 2·68.
0·2020 „ 0·2446 CO_2 „ 0·0514 H_2O. C = 33·02; H = 2·82.
0·0781 „ 10·0 c.c. N_2 at 22° and 756 mm. N = 14·56.
0·2178 „ 0·2570 $BaSO_4$. S = 16·20.
0·1930 „ 0·2356 $BaSO_4$. S = 16·76.
$C_{10}H_8O_8N_4S_2,\frac{1}{2}C_2H_6O$ requires C = 33·08; H = 2·75; N = 14·03; S = 16·04 per cent.

The bisdiazonium sulphate readily dissolved in water to a clear yellow solution, which was employed in the production of the following diazonium salts.

*Naphthalene-*2 : 7-*bisdiazonium platinichloride*,
$C_{10}H_6[N_2]_2PtCl_6,2H_2O$,
separated as a brownish-yellow, crystalline precipitate on adding

aqueous chloroplatinic acid to the solution of the bisdiazonium sulphate. The air-dried salt was not explosive, and could be warmed without decomposition:

0·1378 gave 0·0964 CO_2 and 0·0244 H_2O. C=19·08; H=1·96.
0·1760 „ 0·1243 CO_2 „ 0·0269 H_2O. C=19·26; H=1·70.
0·2170 „ 18·0 c.c. N_2 at 22° and 756 mm. N=9·42.
0·1542 „ 0·2122 AgCl. Cl=34·02.
0·1872 „ 0·0594 Pt. Pt=31·73.
0·1888 lost 0·0114 H_2O at 70—80°. H_2O=6·04.
$C_{10}H_6N_4Cl_6Pt,2H_2O$ requires C=19·16; H=1·59; N=8·94; Cl=34·02; Pt=31·15; H_2O=5·75 per cent.

Naphthalene-2:7-bisdiazonium aurichloride, $C_{10}H_6(N_2\cdot AuCl_4)_2$, was obtained as a reddish-brown, crystalline precipitate on mixing aqueous solutions of chloroauric acid and the bisdiazonium sulphate. The aurichloride was very soluble in alcohol, and even dissolved slightly in ether:

0·1799 gave 0·0936 CO_2 and 0·0172 H_2O. C=14·19; H=1·06.
0·3118 „ 18·5 c.c. N_2 at 20·5° and 760 mm. N=6·77.
0·1290 „ 7·7 c.c. N_2 „ 20·5° „ 758 mm. N=6·79.
0·1620 „ 0·2170 AgCl. Cl=33·15.
0·1834 „ 0·0834 Au. Au=45·47.
$C_{10}H_6N_4Cl_8Au$ requires C=13·95; H=0·69; N=6·51; Cl=33·02; Au=45·81 per cent.

Naphthalene-2:7-bisdiazonium dichromate, $C_{10}H_6[N_2]_2Cr_2O_7$, separated either in reddish-brown leaflets or brown, nodular crystals on adding chromic acid or sodium dichromate to a dilute solution of the bisdiazonium sulphate:

0·2184 gave 24·4 c.c. N_2 at N.T.P. and 0·0824 Cr_2O_3. N=14·07; Cr=25·81.
$C_{10}H_6O_7N_4Cr_2$ requires H=14·07; Cr=26·13 per cent.

The bisdiazonium dichromate is extremely explosive, and detonates with a bright flash when gently heated or even on rubbing.

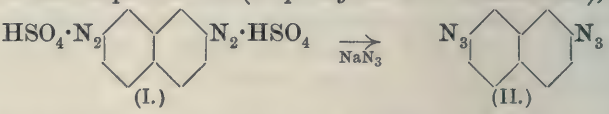
The bisdiazonium sulphate gave rise to sparingly soluble diazo-derivatives when added to aqueous solutions of alkali vanadates, molybdates, and tungstates.

The Sandmeyer Reaction with the Bisdiazonium Salts of 2:7-Naphthylenediamine.

The purified naphthalene-2:7-bisdiazonium sulphate (carefully freed from any excess of nitrous acid) was dissolved in water and added to a hydrochloric acid solution of cuprous chloride. 2:7-Dichloronaphthalene separated immediately, and was purified by sublimation, when it melted at 114—115°, and did not depress the melting point of a specimen prepared from naphthalene-2: 7-disulphonic acid, for which the authors are indebted to Professor Armstrong.

This Sandmeyer reaction gave the same result when repeated with the other bisdiazonium salts of 2: 7-naphthylenediamine.

2: 7-*Bistriazonaphthalene* (*Naphthylene*-2: 7-*bisazoimide*),



2: 7-*Bistriazonaphthalene* (II) was obtained as a brownish-white precipitate on adding sodium azide to a well-cooled aqueous solution of the bisdiazonium sulphate which had been carefully freed from nitrous acid. The product crystallised from petroleum (b. p. 60—80°) in almost colourless leaflets or tabular prisms, which reddened on exposure to light; it melted at 98°:

0·1984 gave 0·4158 CO_2 and 0·0569 H_2O. C = 57·14; H = 3·18.
0·0784 „ 27·0 c.c. N_2 at 22° and 760 mm. N = 39·84.
$C_{10}H_6N_6$ requires C = 57·14; H = 2·85; N = 40·00 per cent.

2: 7-Bistriazonaphthalene has a characteristic odour, recalling that of β-ethoxynaphthalene; it can be partly decolorised by boiling with methyl alcohol and animal charcoal, and crystallises from this solvent in very pale pink plates. Cold concentrated sulphuric acid decomposes the bistriazo-compound with effervescence.

The decomposition of the bisdiazonium sulphate with sodium azide is practically quantitative, and as 2: 7-bistriazonaphthalene is only very sparingly soluble in water, its amount can be determined:

0·1398 $C_{10}H_6(N_2{\cdot}HSO_4)_2,\frac{1}{2}C_2H_5{\cdot}OH$ gave 0·0741 $C_{10}H_6(N_3)_2$, melting at 98°, whereas the calculated amount is 0·0736.

The aqueous filtrate from the precipitated bistriazo-compound, which contained the alcohol of crystallisation of the bisdiazonium sulphate, gave a distinct iodoform reaction, thus confirming the analytical data for this salt.

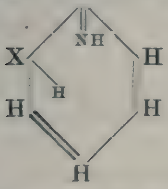
THEORETICAL CONSIDERATIONS.

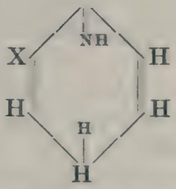
The fact that the 2-aminonaphthalene-7-diazonium salts isolated by Kaufler and Karrer (*loc. cit.*) and the naphthalene-2: 7-bisdiazonium sulphate described above are yellow compounds affords additional evidence in favour of the view that diazonium salts of normal constitution display colour when their diazo-complexes are associated with polynuclear hydrocarbon radicles (compare this vol., p. 1691).

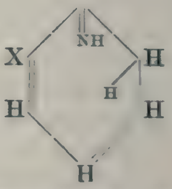
The successive diazotisation of 2: 7-naphthylenediamine salts in two stages is of interest in connexion with the authors' views on the constitution of diazonium salts.

In the first place, it should be noted that all the available evidence strongly supports the assumption that the diazotisability of a base depends on the association of its amino-group with an unsaturated organic complex. This complex need not necessarily be aromatic or even cyclic, but it is, apparently, essential that this group should be unsaturated, for hitherto no amine possessing a fully saturated radicle has ever been diazotised. The existence of a certain degree of residual affinity is a necessary condition for the production of diazonium salts.

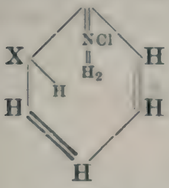
In the aromatic series this residual affinity is supplied by the fourth valency of each carbon atom of the six-membered rings, and the chemical properties which characterise aromatic amines (oxidation, diazotisation, etc.) may be supposed to arise from the interaction of these bases in their tautomeric forms (compare Cain, Trans., 1907, **91**, 1051).

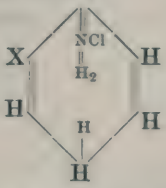


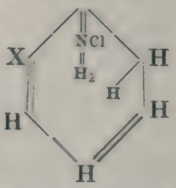




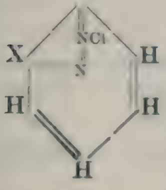
It cannot be too strongly emphasised that diazotisation is a process which takes place only with the undissociated salt of an amine, and not with the base itself. Accordingly, the nitrous acid reacts with the salts (for example, the hydrochloride) of the base in the following tautomeric forms:

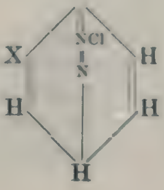


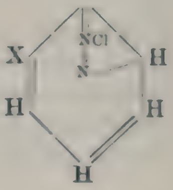




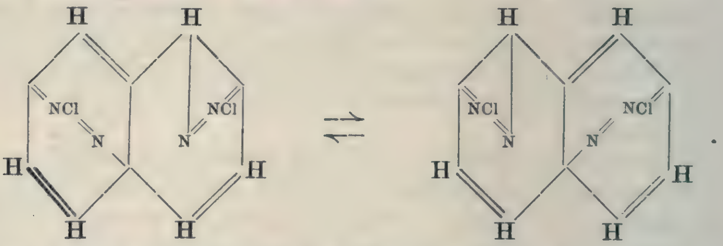
Regarded in this way, diazotisation, which consists in the replacement of three labile hydrogen atoms by nitrogen, leads naturally to the formation of three tautomeric forms of the diazonium chloride:







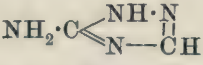
In the special case of the salts of 2:7-naphthylenediamine, the progressive diazotisation arises probably from the circumstance that the two diazonium complexes represent two phases of the diazo-configuration. If the first formed diazonium complex has the para-hemiquinoid structure, then the second will be in the ortho-hemiquinoid phase, and vice versa:



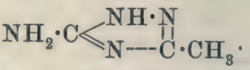
The foregoing hypothesis of the constitution of diazonium salts is based on the assumption that the aromatic amines and their salts are able to react in the tautomeric imino-forms, a change which is possible only when the organic complex associated with the amino-group is unsaturated.

Tautomeric change to the imino-form is possible in the following non-aromatic amines, all of which have manifested to some extent the property of diazotisability:

The aminotriazoles (Thiele and Manchot, *Annalen*, 1898, **303**, 33):

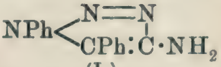


$NH_2\cdot C<\begin{matrix}NH\cdot N\\ \| \\ N{-}{-}CH\end{matrix}$



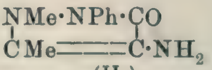
$NH_2\cdot C<\begin{matrix}NH\cdot N\\ \| \\ N{-}{-}C\cdot CH_3\end{matrix}$.

4-Amino-1:5-diphenyl-1:2:3-triazole (Dimroth, Frisoni, and Marshall, *Ber.*, 1906, **39**, 2925) and aminoantipyrine (Knorr and Stolz, *Annalen*, 1896, **293**, 67), represented respectively by formulæ I and II:



$NPh<\begin{matrix}N{=}N\\ | \\ CPh{:}C\cdot NH_2\end{matrix}$

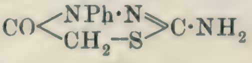
(I.)



$\begin{matrix}NMe\cdot NPh\cdot CO\\ | \qquad\qquad | \\ CMe{=}{=}{=}C\cdot NH_2\end{matrix}$

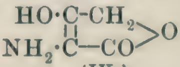
(II.)

Aminophenylpyrithiazinone (Harries and Klamt, *Ber.*, 1900, **33**, 1158) and aminotetronic anhydride (Wolff and Lüttringhaus, *Annalen*, 1900, **312**, 133), with formulæ III and IV:



$CO<\begin{matrix}NPh\cdot N\\ CH_2{-}S\end{matrix}>C\cdot NH_2$

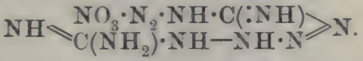
(III.)



$\begin{matrix}HO\cdot C{-}CH_2\\ \| \\ NH_2\cdot C{-}CO\end{matrix}>O$

(IV.)

In addition to these non-aromatic amines, in which the amino-group is associated with a cyclic structure, an interesting extension of the diazo-reaction has recently been discovered by K. A. Hofmann, H. Hock, and R. Roth (*Ber.*, 1910, **43**, 682, 1087), who find that under certain conditions aminoguanidine furnishes diazonium salts, derived, however, not from salts of the base itself, but from a more complex molecule containing two guanidine residues and having a greater degree of unsaturation. The diazonium nitrate, for example, is represented by the formula:

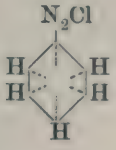


$$\mathrm{NH}{<}\begin{array}{l}\mathrm{NO_3\cdot N_2\cdot NH\cdot C(:NH)}\\ \mathrm{C(NH_2)\cdot NH{-}NH\cdot N}\end{array}{\gg}\mathrm{N}.$$

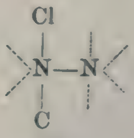
Even in this compound it is possible to discern in the three double linkings a certain analogy to the aromatic diazonium salts.

A further extension of the hypothesis that the diazotisability of an amine depends on the presence in its molecule of an unsaturated group may be put forward to explain why the tendency to form diazonium salts is greatest among aromatic amines.

In the aromatic series, unsaturation of the hydrocarbon radicle is due to the fourth valency of each carbon atom of a six-membered ring. In the diazonium complex, three valencies of one of the two nitrogen atoms are employed as follows: one furnishes the attachment to an acid radicle; another links the diazo-group with a carbon atom of the ring; and the third forms one of the bonds of attachment to the second nitrogen atom. Regarding nitrogen as always potentially quinquevalent, an assumption which is justified by the position of this element in the periodic classification, then the diazonium complex itself, like the aromatic nucleus, has also an unsaturation represented by six valencies. These two sets of six valencies, representing respectively the residual affinities of the aromatic and diazonium complexes, are indicated by dotted lines in formulæ V and VI, the first of which is the well-known centric formula:



(V.)



(VI.)

The authors' view is that maximum stability of the diazonium salt results when the residual affinities of the organic radicle and the diazonium complex satisfy each other to the fullest extent. In an aromatic monodiazonium salt, the residual affinity of the diazo-group is available for saturating the six fourth valencies of the aromatic ring.

This conception of the constitution of diazonium salts suggests, also, an explanation of the following facts: (1) the relative instability of the bisdiazonium salts of homonuclear aromatic diamines; (2) the difficulty sometimes experienced in diazotising completely the salts of these diamines.

The authors desire to express their thanks to the Research Grant Committees of the Royal Society and Chemical Society for grants which have partly defrayed the expenses of this investigation.

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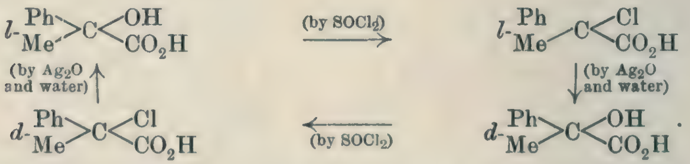
CCLXII.—*Experiments on the Walden Inversion. Part VI. Conversion of the Optically Active α-Hydroxy-α-phenylpropionic Acids into α-Chloro-α-phenylpropionic Acids.*

By Alex. McKenzie and George William Clough.

The authors showed in a former paper (Trans., 1910, **97**, 1016) that when *l*-α-hydroxy-α-phenylpropionic acid was acted on by thionyl chloride at the ordinary temperature there was no evidence that the carboxyl group had been attacked, whereas the hydroxy-group in direct attachment to the asymmetric carbon atom was displaced by the chlorine atom with great readiness.* By this method *l*- and *d*-α-chloro-α-phenylpropionic acids were easily obtained in a state of optical purity, and the interconversion of the optically active α-hydroxy-α-phenylpropionic acids was brought about by aid of the Walden inversion, thus:



$$\begin{tikzcd}
l\text{-}{}^{\text{Ph}}_{\text{Me}}{>}\text{C}{<}^{\text{OH}}_{\text{CO}_2\text{H}} \arrow[r, "\text{(by SOCl}_2\text{)}"] & l\text{-}{}^{\text{Ph}}_{\text{Me}}{>}\text{C}{<}^{\text{Cl}}_{\text{CO}_2\text{H}} \arrow[d, "\text{(by Ag}_2\text{O and water)}"] \\
d\text{-}{}^{\text{Ph}}_{\text{Me}}{>}\text{C}{<}^{\text{Cl}}_{\text{CO}_2\text{H}} \arrow[u, "\text{(by Ag}_2\text{O and water)}"] & d\text{-}{}^{\text{Ph}}_{\text{Me}}{>}\text{C}{<}^{\text{OH}}_{\text{CO}_2\text{H}} \arrow[l, "\text{(by SOCl}_2\text{)}"]
\end{tikzcd}$$

The results obtained by a further study of this subject are placed on record in the present communication.

When the action of thionyl chloride on *l*-α-hydroxy-α-phenylpropionic acid is conducted in such a manner that both hydroxy-groups are displaced by chlorine, the resulting chloro-acid chloride is *laevorotatory*, and on decomposition with acetone containing a little water it gives *l*-α-chloro-α-phenylpropionic acid. The interconversion of the active hydroxy-acids can be carried out according to the scheme:

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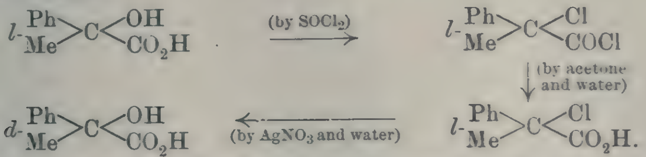
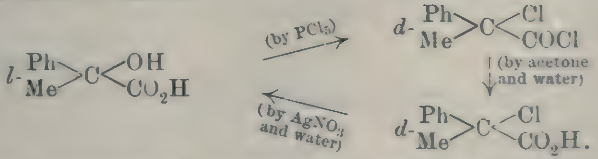
* Later, Stollé (*Ber.*, 1910, **43**, 2471) observed that benzilic acid is converted into diphenylchloroacetic acid in a similar manner when its solution in carbon tetrachloride is acted on by thionyl chloride at the ordinary temperature.



On the other hand, when *l*-α-hydroxy-α-phenylpropionic acid is acted on by phosphorus pentachloride, a change of sign of rotation occurs; the chloro-acid chloride is in this case *dextrorotatory*, and it gives *d*-α-chloro-α-phenylpropionic acid when it is decomposed by aqueous acetone. When the chlorine in the latter product is displaced by the hydroxy-group by aqueous silver nitrate, the parent α-hydroxy-α-phenylpropionic acid is regenerated. The following cycle can thus be effected:



Thionyl chloride and phosphorus pentachloride thus behave differently towards *l*-α-hydroxy-α-phenylpropionic acid, inasmuch as the former gives the *l*-chloro-acid, whereas the latter gives the *d*-chloro-acid. The action of phosphorus pentachloride is accompanied with a large amount of racemisation.

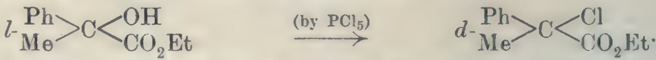
In the course of his work on the Walden inversion, E. Fischer (*Ber.*, 1907, **40**, 489) found that *l*-bromopropionic acid is formed from *d*-alanine by the action of nitrosyl bromide, this action being probably abnormal; when the ester of *d*-alanine, however, is acted on by nitrosyl bromide, the resulting compound is the ester of *d*-bromopropionic acid, thus:

d-alanine → *l*-bromopropionic acid
d-alanine ester → *d*-bromopropionic ester.

The conclusion is drawn that the same reagent (nitrosyl bromide) can act on closely-related substances (for example, acid and ester), in one case normally and in the other case abnormally. This conclusion was borne out when the behaviour of nitrosyl chloride towards active leucine (and its ester) and active aspartic acid (and its ester) was examined. Again, silver oxide, which apparently behaves abnormally in Walden's experiments with the malic acids, can be used to produce either *d*- or *l*-lactic acid from *l*-bromopropionic acid, thus:

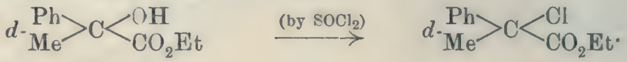
l-bromopropionic acid → *d*-lactic acid.
l-bromopropionylglycine → *l*-lactic acid.

Bearing these results of Fischer in mind, we decided to investigate the action of phosphorus pentachloride and thionyl chloride respectively on the ethyl ester of active α-hydroxy-α-phenylpropionic acid in the hope of throwing some light on the problem as to which of these agents acts abnormally on the hydroxy-acid. The following change, which is accompanied by a large amount of racemisation, takes place when ethyl *l*-α-hydroxy-α-phenylpropionate interacts with phosphorus pentachloride:



$$l\text{-}{}^{\text{Ph}}_{\text{Me}}\!>\!\text{C}\!<^{\text{OH}}_{\text{CO}_2\text{Et}} \xrightarrow{\text{(by PCl}_5\text{)}} d\text{-}{}^{\text{Ph}}_{\text{Me}}\!>\!\text{C}\!<^{\text{Cl}}_{\text{CO}_2\text{Et}}.$$

Unfortunately, the action of thionyl chloride on ethyl *d*-α-hydroxy-α-phenylpropionate does not proceed smoothly, but we have evidence that the following change takes place:



$$d\text{-}{}^{\text{Ph}}_{\text{Me}}\!>\!\text{C}\!<^{\text{OH}}_{\text{CO}_2\text{Et}} \xrightarrow{\text{(by SOCl}_2\text{)}} d\text{-}{}^{\text{Ph}}_{\text{Me}}\!>\!\text{C}\!<^{\text{Cl}}_{\text{CO}_2\text{Et}}.$$

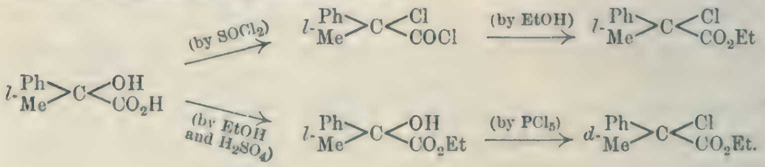
When the changes

$$\begin{cases} l\text{-hydroxy-acid} \xrightarrow{\text{(by PCl}_5\text{)}} \text{-chloro-acid} \\ l\text{-hydroxy-ester} \xrightarrow{\text{(by PCl}_5\text{)}} d\text{-chloro-ester} \end{cases}$$

$$\begin{cases} l\text{-hydroxy-acid} \xrightarrow{\text{(by SOCl}_2\text{)}} l\text{-chloro-acid} \\ l\text{-hydroxy-ester} \xrightarrow{\text{(by SOCl}_2\text{)}} l\text{-chloro-ester} \end{cases}$$

are contrasted, it will be seen that no conclusion can be drawn from them as to which of the agents, thionyl chloride or phosphorus pentachloride, causes the Walden inversion when it acts on the hydroxy-acid.

It was obviously desirable to prove that the *l*-chloro-acid corresponds in configuration with the *l*-chloro-ester. This was done by showing that the *l*-chloro-acid chloride (which gives the *l*-chloro-acid on treatment with aqueous acetone) is converted into the *l*-chloro-ester on addition to ethyl alcohol, the sign of rotation remaining unchanged. It is accordingly possible to convert *l*-α-hydroxy-α-phenylpropionic acid into either ethyl *l*- or ethyl *d*-α-chloro-α-phenylpropionate, thus:



EXPERIMENTAL.

Action of Thionyl Chloride on l-*α-Hydroxy-α-phenylpropionic Acid.*

A mixture of *l*-α-hydroxy-α-phenylpropionic acid (6 grams), prepared by the resolution of the *r*-acid with morphine (*loc. cit.*), and thionyl chloride (20 grams) was kept at the ordinary temperature for two days, and then heated at 80° for one hour. Five grams of a *laevorotatory* acid chloride boiling at 108—110°/10 mm. were obtained. It was added to a mixture of acetone (20 c.c.) and water (1 c.c.), and after a day the solvent was removed at the ordinary temperature under diminished pressure. The crude chloro-acid (3 grams) was crystallised once from light petroleum, when the pure *l*-acid (*loc. cit.*) was obtained, melting at 71—72°, and having the following specific rotation in benzene solution:

$$l=2,\ c=7{\cdot}188,\ \alpha_D-3{\cdot}78^\circ,\ [\alpha]_D-26{\cdot}3^\circ.$$

This acid gave a dextrorotatory mixture of α-hydroxy-α-phenylpropionic acids when the displacement of chlorine was effected by aid of aqueous silver nitrate.

It is thus possible to prepare optically pure *l*-α-chloro-α-phenylpropionic acid even when the temperature of the action with thionyl chloride is raised so that the carboxyl group of the hydroxy-acid is displaced.

The lævorotation of the chloro-chloride, prepared from 6 grams of the *l*-hydroxy-acid and 28 grams of thionyl chloride under temperature conditions somewhat different from the preceding, was confirmed. One gram of the chloro-chloride was added to 7 c.c. of acetone, and the solution gave $\alpha_D-4{\cdot}5^\circ$ in a 1-dcm. tube.

Action of Phosphorus Pentachloride on l- *and* d-*α-Hydroxy-α-phenylpropionic Acids.*

A mixture of *l*-α-hydroxy-α-phenylpropionic acid (12 grams) and the calculated amount of phosphorus pentachloride (30 grams) was maintained at 15° for thirty minutes, by which time the vigorous evolution of hydrogen chloride had subsided. On heating to 70°, a brisk action again took place; the temperature was raised from 70° to 100° within thirty minutes, and finally maintained at 100° for one hour. The action of the phosphorus pentachloride apparently took place in two distinct stages. The phosphoryl chloride was removed, and the residual oil fractionated under diminished pressure. Six grams of a colourless oil, boiling at 113—115°/15 mm., were obtained. This chloro-acid chloride was *dextrorotatory*, giving $\alpha_D+3{\cdot}10^\circ$ in a 1-dcm. tube, and its solution in acetone was also dextrorotatory. It was added to a mixture of acetone (20 c.c.) and water (1 c.c.). Next day, the solvent was removed at the ordinary temperature under diminished pressure, and the residual solid drained on porous earthenware. It amounted to 4 grams, melted at 70—75°, and gave the following value in benzene solution:

$$l=2,\ c=12{\cdot}7,\ \alpha_D+0{\cdot}56^\circ,\ [\alpha]_D+2{\cdot}2^\circ.$$

Found, Cl = 19·2. Calc. Cl = 19·3 per cent.

The resulting acid was thus a mixture of *d*- and *r*-α-chloro-α-phenylpropionic acids, and a change of sign of rotation accordingly took place during the displacement of the chlorine by the hydroxy-group under the following conditions. The acid was shaken for four hours at the ordinary temperature with a solution of 5 grams of silver nitrate in 20 c.c. of water, and the mixture was then boiled for one minute and filtered. The hydroxy-acid was extracted with ether. It melted at 88—90°, was free from chlorine, and was lævorotatory. In ethyl-alcoholic solution:

$$l=4,\ c=9{\cdot}58,\ \alpha_D-0{\cdot}67^\circ,\ [\alpha]_D-1{\cdot}7^\circ.$$

The action of phosphorus pentachloride (25 grams) on *d*-α-hydroxy-α-phenylpropionic acid (10 grams) was also studied under conditions similar to the preceding. The chloro-acid chloride was in this case lævorotatory. On decomposition with aqueous acetone it gave a mixture of *l*- and *r*-α-chloro-α-phenylpropionic acids.

Conversion of l-*α-Chloro-α-phenylpropionyl Chloride into Ethyl* l-*α-Chloro-α-phenylpropionate.*

The lævorotatory α-chloro-α-phenylpropionyl chloride, prepared from *l*-α-hydroxy-α-phenylpropionic acid (10 grams) and thionyl chloride (28 grams), was added to ethyl alcohol and the product fractionated. The ester was a *lævorotatory* oil; it amounted to 4 grams, boiled at 131—132°/18 mm., and gave the following values:

$$l=1,\ \alpha_D^{17}-6{\cdot}30^\circ,\ D_4^{17}\ 1{\cdot}124,\ [\alpha]_D^{17}\ -5{\cdot}6^\circ.$$

Found, Cl = 16·8. $C_{11}H_{13}O_2Cl$ requires Cl = 16·7 per cent.

We have no evidence that this ester was optically pure, and it is necessary to bear in mind that partial racemisation occurs very frequently when the alcoholic hydroxy-group of an optically active hydroxy-carboxylic acid is displaced by halogen.

It appeared from the following experiment that this ester corresponds in configuration with *l*-α-chloro-α-phenylpropionic acid. The ester (3 grams) was added to 25 c.c. of *N*-aqueous silver nitrate, and maintained at the ordinary temperature for twenty-four hours. The silver chloride was removed, and the filtrate boiled with aqueous potassium hydroxide until all the oil had disappeared. The resulting α-hydroxy-α-phenylpropionic acid obtained by acidification and extraction with ether amounted to 2 grams, melted at 84—89°, and was dextrorotatory in ethyl-alcoholic solution:

$$l=2,\ c=18{\cdot}48,\ \alpha_D+1{\cdot}33^\circ,\ [\alpha]_D+3{\cdot}6^\circ.$$

Action of Phosphorus Pentachloride and of Thionyl Chloride on the Optically Active Ethyl α-Hydroxy-α-phenylpropionates.

Ethyl l-*α-hydroxy-α-phenylpropionate*, $OH·CMePh·CO_2Et$, prepared by the esterification of *l*-α-hydroxy-α-phenylpropionic acid by ethyl alcohol and sulphuric acid, is an oil boiling at 127°/12 mm.:

0·1330 gave 0·3322 CO_2 and 0·0865 H_2O. C = 68·1; H = 7·3.
$C_{11}H_{14}O_3$ requires C = 68·0; H = 7·3 per cent.

It has D_4^{13} 1·097 and α_D^{13} $-29·24°$ $(l=1)$; whence $[\alpha]_D^{13}$ $-26·7°$.

When this ester is acted on by phosphorus pentachloride, the resulting ethyl α-chloro-α-phenylpropionate is *dextrorotatory*, but it is impossible to prevent a large amount of racemisation taking place in this change. Powdered phosphorus pentachloride (7 grams) was added gradually within an interval of one hour to the *l*-hydroxy-ester (6 grams). After three hours at the ordinary temperature the product was warmed at 30° for a few minutes, when no further action was perceptible. It was then treated with ether and ice, and the ethyl α-chloro-α-phenylpropionate isolated as an oil, boiling at 138—139°/28 mm.:

Found, Cl = 16·5. $C_{11}H_{13}O_2Cl$ requires Cl = 16·7 per cent.

The ester had α_D $+1·10°$ in a 1-dcm tube.

On decomposing it with a slight excess of 1·03*N*-aqueous sodium hydroxide, the displacement of the chlorine by the hydroxy-group of course accompanied the saponification; the product of the action was *r*-α-hydroxy-α-phenylpropionic acid.

Although attempts to prepare ethyl *dl*-α-chloro-α-phenylpropionate in a state of even approximate purity from ethyl *dl*-α-hydroxy-α-phenylpropionate (b. p. 124—125°/10 mm.) and thionyl chloride met with no success, it was nevertheless decided to examine the action of thionyl chloride on the optically active hydroxy-esters. The material used for this purpose was the dextrorotatory mixture of *d*- and *r*-α-hydroxy-α-phenylpropionic acids obtained from the mother liquors resulting from the morphine resolution of the *r*-acid. It was esterified by ethyl alcohol and sulphuric acid, and the ester obtained had $\alpha_D + 14°$ in a 1-dcm. tube. Twelve grams of this product remained for seven days at the ordinary temperature after having been mixed with 14 grams of thionyl chloride. The liquid was then heated for twenty hours at 50—60°, and for five hours longer at 60—70°, but the action was apparently not quite complete even under these conditions. The product was fractionated, and an oil boiling at 138—141°/25 mm. was obtained; it was *dextrorotatory*, giving α_D $+1·50°$ in a 1-dcm. tube. It contained, however, only 11·7 per cent. of chlorine. We were able to draw the conclusion, however, from the following experiment that *d*-α-chloro-α-phenylpropionate was actually present in this impure product. The chlorine in it was first displaced by aqueous silver nitrate, and the product then saponified with aqueous potassium hydroxide. The resulting potassium salt was *laevorotatory* in aqueous solution, and the α-hydroxy-α-phenylpropionic acid obtained from it was also *laevorotatory*. This result was confirmed by a second experiment.

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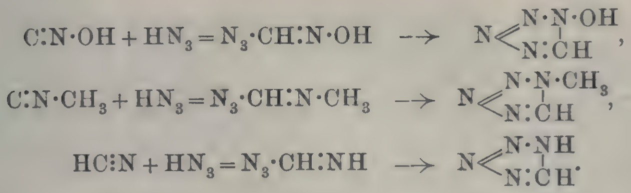
CCLXIII.—*The Triazo-group. Part XV. Triazoethylene (Vinylazoimide) and the Triazoethyl Halides.*

By MARTIN ONSLOW FORSTER and SIDNEY HERBERT NEWMAN.

MANY cases have now been placed on record in which the atoms composing a triazo-group in the neighbourhood of an unsaturated linking have lent themselves to the formation of a cycloid, owing to a change involving saturation of this linking by the members of the azoimide nucleus. As recent examples of this principle may be quoted the spontaneous transformation of allylazoimide into an isomeric diazoamino-compound (Trans., 1908, **93**, 1174), whilst an attempt to prepare benzhydroximic azide by interaction of the chloride and sodium azide led to 1-hydroxy-5-phenyltetrazole (Trans., 1909, **95**, 183; compare also Wieland, *Ber.*, 1909, **42**, 4199).

In the cases mentioned above, and in others which might be indicated, the environment favourable to the display of additive functions on the part of the triazo-group is intramolecular. Whether it is necessarily so cannot be stated with confidence, because, although striking examples of apparently intermolecular addition have been furnished quite recently by Palazzo and Oliveri-Mandalà (*Atti R. Accad. Lincei*, 1910, [v], **19**, i, 218, 228), who found that hydrazoic acid converts fulminic acid and methylcarbylamine into 1-hydroxytetrazole and 1-methyltetrazole respectively, whilst Dimroth and Fester (*Ber.*, 1910, **43**, 2219) showed that tetrazole itself is obtainable by the interaction of hydrazoic and prussic acids, it is nevertheless possible that these changes actually depend on preliminary addition of H and N_3 to unsaturated atoms, and that it is the resulting triazo-compound which undergoes intramolecular rearrangement, as follows:

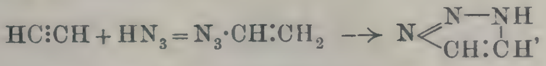


$$\mathrm{C{:}N\cdot OH + HN_3 = N_3\cdot CH{:}N\cdot OH} \longrightarrow \mathrm{N}\!\left<\begin{matrix}\mathrm{N\cdot N\cdot OH}\\ \mathrm{N{:}CH}\end{matrix}\right.,$$

$$\mathrm{C{:}N\cdot CH_3 + HN_3 = N_3\cdot CH{:}N\cdot CH_3} \longrightarrow \mathrm{N}\!\left<\begin{matrix}\mathrm{N\cdot N\cdot CH_3}\\ \mathrm{N{:}CH}\end{matrix}\right.,$$

$$\mathrm{HC{\vdots}N + HN_3 = N_3\cdot CH{:}NH} \longrightarrow \mathrm{N}\!\left<\begin{matrix}\mathrm{N\cdot NH}\\ \mathrm{N{:}CH}\end{matrix}\right..$$

In addition to the experiment just mentioned, Dimroth and Fester caused hydrazoic acid to act on acetylene, and although 1 : 2 : 3-triazole was obtained therefrom, they do not classify this change with the foregoing ones, as depending on the intermediate formation of vinylazoimide,



$$\mathrm{HC{\vdots}CH + HN_3 = N_3\cdot CH{:}CH_2} \longrightarrow \mathrm{N}\!\left<\begin{matrix}\mathrm{N{-}NH}\\ \mathrm{CH{:}CH}\end{matrix}\right.,$$

because phenylazoimide is converted into 1-phenyl-2 : 3-triazole by the action of acetylene. As we have been engaged for some time in experiments leading to the preparation of vinylazoimide, we think it may be of interest to put forward a description of this substance, which was isolated with the object of studying its tendency to undergo the above rearrangement.

The first experiments in the direction indicated were begun more than two years ago in continuation of the work on allylazoimide. Attempts were made to bring vinyl bromide into double decomposition with sodium azide, but there was not any evidence of the change having taken place; in spite of the readiness with which usually the triazo-group may be substituted for halogen in aliphatic compounds, the failure was not surprising, as it is well known that halogen attached to unsaturated carbon takes part in such reactions with the greatest difficulty. The preparation of triazoethyl alcohol (Trans., 1908, **93**, 1865), however, suggested the possibility of arriving at triazoethylene (vinylazoimide) by the withdrawal of halogen hydride from a triazoethyl halide. Accordingly, triazoethyl alcohol was converted into triazoethyl bromide by the action of phosphorus tribromide, and then by double decomposition with sodium iodide, triazoethyl iodide was prepared from the bromide; on acting with alcoholic potassium hydroxide on these compounds, they were readily deprived of halogen hydride without affecting the triazo-group.

Triazoethylene is a pale yellow liquid, heavier than water, boiling at 26°, and having an odour suggesting that of ethylene itself. It decolorises bromine water without delay, forming a heavy, oily dibromide. At one time we entertained the hope that it might be possible to withdraw the elements of hydrogen bromide from this substance in such a way as to produce triazoacetylene, the copper derivative of which would probably rank among violent explosives, but it was soon found that the dibromide itself is a dangerous material, and, moreover, breaks up in an interesting manner under the influence of water. When suspended therein, the oil rapidly disappears, hydrobromic and hydrazoic acids being set free, whilst bromoacetaldehyde remains dissolved:

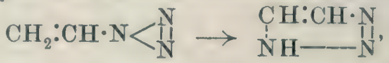
$$CH_2Br{\cdot}CHBr{\cdot}N_3 + 2H_2O = HBr + HN_3 + CH_2Br{\cdot}CH(OH)_2 \longrightarrow CH_2Br{\cdot}CH{:}O + H_2O.$$

So far as we know, the dibromide of triazoethylene is the first compound in which a triazo-group is attached to an atom of carbon which carries also a halogen, and its peculiar susceptibility towards water explains the subsidiary decomposition which has always been observed to accompany the production of a bistriazo-compound from the double decomposition of sodium azide and a dihalogen derivative of the aliphatic series in which both halogen atoms are attached to the same atom of carbon (Trans., 1908, **93**, 1070; also this vol., pp. 126 and 1360). We have not attempted to isolate and distil the substance, because a brief experience of *αα*-bistriazoethane, which exploded with great violence at the laboratory temperature, apparently spontaneously, renders it most probable that *αβ*-dibromo-*α*-triazoethane would behave in the same way. This seems the more likely to take place in view of the possibility that the decomposition of triazoethylene dibromide might follow a different course in absence of water, leading to bromoazoimide:

$$CH_2Br{\cdot}CHBr{\cdot}N_3 \longrightarrow BrN_3 + CH_2Br{\cdot}CH \longrightarrow CHBr{:}CH_2.$$

Since Raschig has shown (*Ber.*, 1908, **41**, 4194) that chloroazoimide is frightfully explosive, the foregoing possibility is discouraging to a further investigation of *αβ*-dibromo-*α*-triazoethane.

The original purpose with which triazoethylene was prepared, namely, to illustrate its transformation into triazole:



$$CH_2{:}CH{\cdot}N{<}\begin{array}{c}N\\ ||\\ N\end{array} \longrightarrow \begin{array}{l}CH{:}CH{\cdot}N\\ \quad\quad\quad\quad ||\\ NH——N\end{array},$$

has not been fulfilled, the substance having shown itself to be surprisingly stable. After being heated with dilute alcohol under reflux during twelve hours, a considerable proportion was found to have survived, and although the remainder had changed into a dark brown substance, the presence of triazole could not be established. Furthermore, on heating an alcoholic solution in a sealed tube during twelve hours at 100—110°, there was produced a dark brown liquid having the odour of a carbylamine, and giving a precipitate with mercuric chloride, but again it was not found possible to recognise triazole.

The pale yellow colour of triazoethylene is an interesting feature of the compound, and appears to be a genuine property, because it has been noticed in every specimen, whether prepared from triazoethyl iodide or bromide. It is doubtless due to the concentration of unsaturated atoms in a small molecule, and although not so intense as that of diazomethane, it is nevertheless quite distinctive. The comparatively high boiling point was not expected, because the recorded boiling points of vinyl chloride and of vinyl bromide are −15° and +16° respectively, and without having made a study of the subject, we were under the impression that, whilst the boiling point of an aliphatic chloro-derivative is unquestionably lower than that of the corresponding triazo-compound, the latter would be more volatile than the brominated substance. As it is often a matter of considerable practical importance to be able to predict, roughly, the boiling point of a new triazo-compound from that of its haloid parent, we have taken afresh the boiling point of several typical aliphatic azoimides described in previous papers, side by side with those of the corresponding bromo-derivatives. The results show conclusively that the triazo-group exerts an elevating effect on the boiling point greater than that of the bromine atom.

		B. p.	Mm.
Vinyl bromide	$CH_2:CHBr$	16°	750
Vinylazoimide	$CH_2:CHN_3$	26	760
Ethylene dibromide	$CH_2Br·CH_2Br$	37	20
Triazoethyl bromide	$CH_2Br·CH_2N_3$	49	20
Ethyl α-bromopropionate	$CH_3·CHBr·CO_2Et$	61	16
,, α-triazopropionate	$CH_3·CHN_3·CO_2Et$	70	16
,, α-bromo*iso*butyrate	$CBr(CH_3)_2·CO_2Et$	62	16
,, α-triazo*iso*butyrate	$CN_3(CH_3)_2·CO_2Et$	71	16
,, α-bromo*iso*valerate	$CH(CH_3)_2·CHBr·CO_2Et$	79	16
,, α-triazo*iso*valerate	$CH(CH_3)_2·CHN_3·CO_2Et$	82	16

The relationship between the triazo-group and the chlorine atom as regards their effect on the boiling point is revealed by the following data:

		B. p.	Mm.
Vinyl chloride	$CH_2:CHCl$	−15°	760
Vinylazoimide	$CH_2:CHN_3$	26	760
β-Chloroethyl alcohol	$CH_2Cl·CH_2·OH$	44	20
β-Triazoethyl ,,	$CH_2N_3·CH_2·OH$	73	20
Ethyl chloroformate	$Cl·CO_2Et$	93	760
,, triazoformate	$N_3·CO_2Et$	114	769
,, chloroacetate	$CH_2Cl·CO_2Et$	52	20
,, triazoacetate	$CH_2N_3·CO_2Et$	70	20
Methyl α-chloromethylacetoacetate	$CH_3·CO·CCl(CH_3)·CO_2Me$.	76	13
,, α-triazomethylacetoacetate	$CH_3·CO·CN_3(CH_3)·CO_2Me$.	76	0·66

We have not, as yet, been very successful in attempts to utilise triazoethyl iodide as a triazo-ethylating agent. Triazoethyl chloride has been obtained by heating the iodide with dry mercuric chloride, and in this connexion it is worth noting that the bromide remains unchanged when treated with the mercury salt under similar conditions. *iso*Nitrosocamphor was transformed into an oily triazoethyl derivative when heated with triazoethyl iodide and silver oxide in dry ether, but an attempt to prepare bistriazoethyl ether by heating a mixture of triazoethyl alcohol and iodide with dry silver oxide on the water-bath led to the recovery of unaltered triazoethyl alcohol after five days. This is the more curious because the action of ethyl iodide on triazoethyl alcohol in presence of silver oxide leads without difficulty to triazoethyl ether, $C_2H_5\cdot O\cdot CH_2\cdot CH_2N_3$. Lastly, we have not been able to produce triazoethylcarbimide by the action of triazoethyl iodide on lead or silver cyanate, whilst the interaction of triazoethyl iodide and silver cyanide, although producing an odour of carbylamine, was too far from complete to admit of isolating any definite products.

EXPERIMENTAL.

Triazoethylene (*Vinylazoimide*), $CH_2{:}CHN_3$.

The alcoholic potassium hydroxide used for withdrawing halogen hydride from the triazoethyl halides was a solution of 5 grams in 20 grams of water, mixed with 25 grams of absolute alcohol. This was heated on steam in a generating flask, into which was fitted a dropping-funnel and a reflux double-surface condenser; from the latter, connexion was made to a small, dry flask, thence to a U-tube filled with calcium chloride, and finally to a large test-tube surrounded by a freezing-mixture. The temperature of the water in the condenser having been adjusted to 30°, 5 grams of triazoethyl iodide was admitted drop by drop into the alcoholic potassium hydroxide at the temperature of boiling alcohol, when a pale yellow liquid gradually accumulated in the small flask between the generator and the U-tube. All the iodide having been added, the liquid was boiled during fifteen minutes, when it was found that the cooled tube also contained some yellow liquid, and this, being presumably free from alcohol and water, was regarded as pure triazoethylene, and found to boil at 26°/760 mm. Although this experiment has been made several times, and triazoethyl bromide has been substituted for the iodide, it has always been observed that the liquid in both condensing vessels is pale yellow, and that the colour does not vary in depth; it therefore seems safe to conclude that this feature is not due to some impurity. Reference has been made to the absence of any conclusive evidence that triazoethylene changes into triazole; in addition to the experiments towards this end which have been already described, a solution of triazoethylene in petroleum was left in a stoppered vessel exposed to light during many days without giving the faintest indication of triazole; on allowing the solvent to evaporate, the odour of a carbylamine was noticeable.

The *dibromide* of triazoethylene was prepared by adding ice-cold bromine water to a well-cooled suspension of the substance in water, the colour of the halogen being immediately destroyed, whilst the limpid vinylazoimide changed to a heavy, viscous oil. It is necessary to be most cautious in adding the halogen, because on one occasion a drop of bromine was admitted by accident to the vessel containing the triazo-compound, and led to a violent explosion, although the amount of material involved could not have exceeded 1 gram, and this was diluted with 20 c.c. of water. On allowing the dibromide to remain in contact with water, it rapidly disappeared, and the liquid was found to contain hydrazoic and hydrobromic acids; moreover, it restored the colour to Schiff's reagent, and when mixed with ammoniacal silver oxide and filtered, the liquid quickly deposited silver on warming. In order to make sure that the decomposition of triazoethylene dibromide by water does not follow the possible alternative course, that, namely, leading to bromoazoimide and vinyl bromide, a specimen of vinylazoimide was converted into the dibromide with a deficit of bromine, and at once treated with dilute sodium hydroxide, in the expectation that if bromoazoimide is formed, it would behave towards alkali in the manner that characterises chloroazoimide, and that alkali hypobromite would be produced; we were able to show that hypobromite is not formed, and therefore conclude that the decomposition proceeds only in the direction of hydrobromic and hydrazoic acids along with bromoacetaldehyde.

The interaction of triazoethylene and concentrated sulphuric acid is mild, gas being evolved slowly, but brisk effervescence occurs with a solution of stannous chloride in hydrochloric acid. The conclusion that alcoholic potassium hydroxide is without action on the substance may be drawn from the fact that on evaporating to dryness the liquid contained in the generating flask, no trace of alkali azide was to be found.

β-Chloro-α-triazoethane (*Triazoethyl Chloride*), $N_3\cdot CH_2\cdot CH_2Cl$.

The first attempts to prepare this material were made by adding triazoethyl alcohol dissolved in absolute ether to the calculated amount of phosphorus pentachloride covered with the same solvent; considerable action took place, and was increased by heating under reflux, but the yield of triazoethyl chloride, being only 2 grams from 20 grams of the alcohol, was too disappointing to encourage the adoption of this method. Thionyl chloride acts vigorously on triazoethyl alcohol, but, as might be expected, gives a product which appears to be triazoethyl sulphite, and triazoethyl chloride could not be detected, whilst the effect of passing dry hydrogen chloride into a suspension of anhydrous zinc chloride in triazoethyl alcohol was to liberate hydrazoic acid. It was not until triazoethyl iodide became available that the preparation of the chloride was possible.

Twenty grams of triazoethyl iodide, mixed with 32 grams of dried mercuric chloride, were heated at 100° during three hours in a small distilling flask, from which the product was then boiled under 25 mm. pressure, 10 grams, or 90 per cent. of the theoretical amount, being obtained; on re-distillation under the same pressure, the substance boiled steadily at 45°:

0·0874 gave 30·9 c.c. N_2 at 24° and 751 mm. $N = 39·16$.
0·2709 „ 0·3642 AgCl. $Cl = 33·25$.

$C_2H_4N_3Cl$ requires $N = 39·81$; $Cl = 33·65$ per cent.

The substance is limpid and colourless, having a pleasant odour suggesting that of chloroform; the density is 1·2885/24°. The action with a solution of stannous chloride in hydrochloric acid is sluggish, gas being evolved only on warming the liquids; the effervescence with concentrated sulphuric acid becomes brisk on stirring, but the triazo-group appears to be indifferent towards alkalis, which only liberate triazoethylene. The chloride does not lose its halogen completely when heated with boiling alcoholic silver nitrate, as is the case with the other triazoethyl halides, and the above estimation of chlorine was made by heating in alcohol with 30 per cent. aqueous potassium hydroxide, followed by precipitation with silver nitrate in the solution acidified by nitric acid.

When thrown on a hot plate, the substance decrepitates, and burns with a violet flame.

β-Bromo-α-triazoethane (*Triazoethyl Bromide*), $N_3·CH_2·CH_2Br$.

Although triazoethyl bromide has been obtained by the action of bromine on triazoethyl alcohol in presence of amorphous phosphorus, this is not the most convenient method of preparation, the interaction of phosphorus tribromide and the alcohol, when moderated by a diluent such as ether or petroleum, leading to more satisfactory results. One hundred grams of triazoethyl alcohol, covered with 100 c.c. of petroleum (b. p. 40°) in a flask surrounded with melting ice, were treated slowly with 112 grams of phosphorus tribromide in 250 c.c. of the same petroleum, the mixture being shaken vigorously after each portion was added; phosphorous acid separated, and a heavy, pale brown, viscous oil, insoluble in petroleum, constituted a large proportion of the product. After three hours on the water-bath under reflux, the less dense liquid was decanted, and the viscous residue shaken several times with small quantities of petroleum, which were added to the decanted solution of triazoethyl bromide; any excess of phosphorus tribromide was destroyed by agitation with small quantities of water, and the liquid having been treated with ignited sodium sulphate, petroleum was boiled away, and the residue distilled under diminished pressure. The best yield obtained by this process was only 58 grams, representing about 34 per cent. of the amount anticipated:

0·0641 gave 15·9 c.c. N_2 at 24° and 765 mm. N = 28·00.
0·4942 „ 0·6198 AgBr. Br = 53·38.

$C_2H_4N_3Br$ requires N = 28·02; Br = 53·33 per cent.

Triazoethyl bromide is a colourless liquid, having the odour of ethylene dibromide, and rapidly becoming yellow when exposed to light; it boils at 49°/20 mm., and has the density 1·6675/19°. Action with concentrated sulphuric acid and with a solution of stannous chloride in hydrochloric acid resembles that of the chloro-compound, but hot alcoholic silver nitrate leads more readily to the elimination of halogen than in the case of that substance, and the above determination of bromine was carried out by this agent. The bromide does not become ignited when thrown on a hot plate, merely decrepitating mildly.

Attempts have been made to identify the viscous, brown oil which accompanies triazoethyl bromide when prepared by the foregoing method, so far without success. It is the production of this substance which is responsible for the disappointing yield, and is particularly inconvenient because triazoethyl bromide is the starting material for the chloride and the iodide. The presence of phosphorus, bromine, and the triazo-group suggested that the substance might be the bromide of bistriazoethylphosphorous acid, $(N_3{\cdot}CH_2{\cdot}CH_2{\cdot}O)_2PBr$, but the bromine content was much too low; it may be a mixture of this substance with triazoethyl phosphite, $(N_3{\cdot}CH_2{\cdot}CH_2{\cdot}O)_3P$, but an attempt to recover triazoethyl alcohol from it by hydrolysis was not successful.

β-Iodo-α-triazoethane (*Triazoethyl Iodide*), $N_3{\cdot}CH_2{\cdot}CH_2I$.

The method employed for this preparation was the one recently described by Finkelstein (*Ber.*, 1910, **43**, 1528), and was found to be expeditious and economical. Fifty-eight grams of triazoethyl bromide were added to a solution of 60 grams of sodium iodide in 400 c.c. of dry acetone, sodium bromide being precipitated immediately; the mixture having remained at the ordinary temperature during the night, action was completed by heating under reflux, when about two-thirds of the solvent was distilled off, and the residue poured into water contained in a separating funnel, from which the heavy, dark brown liquid was then tapped. This was mixed with the ether used for extracting the triazoethyl iodide from the aqueous acetone, and shaken vigorously with a little mercury in order to remove dissolved iodine, the residue from the dried ether being then distilled under diminished pressure, yielding 43 grams:

0·0814 gave 15·5 c.c. N_2 at 23° and 764 mm. N = 21·58.
0·4270 „ 0·5063 AgI. I = 64·12.
$C_2H_4N_3I$ requires N = 21·32; I = 64·45 per cent.

Triazoethyl iodide boils at 68°/20 mm., and when freshly distilled is colourless, but quickly becomes pale red; the odour resembles exactly that of ethyl iodide. It has the density 1·9154/25°, and is able to dissolve mercuric iodide, a property brought to light by the fact that a specimen which had been decolorised by agitation with mercury left a considerable residue of the salt on redistillation. The action with stannous chloride in hydrochloric acid is more brisk than in the case of the other triazoethyl halides, which the iodide resembles, however, in regard to interaction with concentrated sulphuric acid. Behaviour on the hot plate is similar to that of triazoethyl chloride.

It was hoped that a variety of interesting substances might be obtainable from typical compounds containing replaceable hydrogen by triazo-ethylation, but hitherto we have not been successful in this direction. *p*-Nitrophenol, for instance, when heated in dry benzene with silver oxide and triazoethyl iodide, gave a brown oil which did not invite further examination. *iso*Nitrosocamphor also gave an oil, remaining liquid during four months, and containing 22·35 per cent. of nitrogen ($C_{12}H_{18}O_2N_4$ requires N = 22·4 per cent.). Silver and lead cyanates were heated in ether and in benzene at the boiling points of these with triazoethyl iodide during many hours, but triazoethylcarbimide could not be recognised, although in absence of a diluent, some action takes place at about 100°, as indicated by a mild explosion which occurred. Silver cyanide developed the carbylamine odour when heated with triazoethyl iodide during two days on the water-bath, but the proportion of material remaining unchanged at the end of the experiment was too large to hold out any prospect of success. Bistriazoethyl sulphate appears to be formed when triazoethyl iodide is heated in dry benzene with silver sulphate, production of silver iodide being clearly indicated; the residue left by the solvent on evaporation did not distil at 140°/1 mm., but when hydrolysed with 30 per cent. potassium hydroxide, the liquid contained potassium sulphate, unmixed with iodide.

An attempt was made to prepare bistriazoethyl ether by heating 5 grams of triazoethyl alcohol and 11·3 grams of triazoethyl iodide with 15 grams of dry silver oxide on the water-bath during five days, but the entire product distilled at 85°/35 mm., weighed

5 grams, and contained 48·3 per cent. of nitrogen; this is the amount required by triazoethyl alcohol itself, whilst bistriazoethyl ether contains 53·8 per cent., from which it would appear that in the above experiment the triazoethyl alcohol remained unchanged, whilst the triazoethyl iodide was transformed into triazoethylene and diffused out of the apparatus.

β-Triazoethyl Ether, $N_3{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}C_2H_5$.

Twenty grams of triazoethyl alcohol and 50 grams of ethyl iodide were allowed to remain in darkness with 50 grams of dry silver oxide during two days, being then heated on the water-bath with occasional addition of small quantities of ethyl iodide. After one week, the liquid was separated and distilled under diminished pressure:

0·1057 gave 33·5 c.c. N_2 at 21° and 763 mm. N = 36·39.

$C_4H_9ON_3$ requires N = 36·51 per cent.

The substance is a colourless liquid, boiling at 49°/25 mm., and having the density 0·9744/24°. The odour resembles that of chloroether, and in steam is pungent and sweet. With concentrated sulphuric acid or a solution of stannous chloride in hydrochloric acid, there is a vigorous effervescence, but hot concentrated alcoholic potassium hydroxide appears to be without action on triazoether, the azoimide nucleus remaining intact. Triazoethyl ether does not explode when thrown on a hot iron plate. the vapour burning with a luminous, white flame.

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CCLXIV.—*The Intermolecular Condensation of Aromatic Sulphinic Acids. Part I.*

By Thomas Percy Hilditch.

The well-known tendency of aromatic sulphinic acids to enter into combination with other benzenoid residues through the elimination of water is more than maintained in the corresponding acid chlorides, which, as was observed when the latter compounds were originally obtained in a pure condition (Hilditch and Smiles, *Ber.*, 1908, **41**, 4113), are exceedingly reactive and unstable. In the course of some work on the reduction of these chlorides, it was noticed that, if too much heat was applied during their preparation or the subsequent treatment, decomposition set in, and white, crystalline, insoluble compounds, sometimes accompanied by tarry matter, were formed in considerable quantity.

The present communication describes some experiments undertaken to elucidate the nature of these by-products. It was found that by heating benzenesulphinyl chloride, $C_6H_5{\cdot}SOCl$, or *p*-toluenesulphinyl chloride, $C_6H_4Me{\cdot}SOCl$, either alone at 100° or in boiling chloroform, or in presence of a slight excess of thionyl chloride beyond that needed for the preparation of the acid chlorides, a semi-solid, dark-coloured mass was obtained, from which the various compounds formed were separated by successive extraction with light petroleum, alcohol, and toluene. Furthermore, in order to avoid the formation of tarry decomposition products when heat was applied, the condensing action of cold concentrated sulphuric acid on these two chlorides was investigated, and analogous products were obtained, whilst, finally, it was established that the free sulphinic acid, when left for a sufficient length of time in solution in cold concentrated sulphuric acid, underwent a similar change, and from experiments with a number of aromatic sulphinic acids it appeared that the course of the reaction was conditioned largely by the substituents present in the benzene nucleus.

From a general point of view, it would appear that besides simple oxidation to sulphonic acids there are the following possibilities to be considered in this decomposition of sulphinic acids:

(i) The usual formation of disulphoxides, with possible further decomposition of the latter substances:

$$3C_6H_5{\cdot}SO_2H = C_6H_5{\cdot}SO_3H + C_6H_5{\cdot}S_2O_2{\cdot}C_6H_5.$$

(ii) (*a*) Intermolecular condensation of the sulphinic acids, possibly involving more than two molecules of the acid, but not proceeding beyond the sulphoxide stage; for example:

$$3C_6H_5{\cdot}SO_2H \longrightarrow C_6H_5{\cdot}SO{\cdot}C_6H_4{\cdot}SO{\cdot}C_6H_4{\cdot}SO_2H.$$

(*b*) Further intermolecular condensation of the sulphoxides to complex sulphonium bases (compare Smiles and Le Rossignol, Trans., 1906, **89**, 696; 1908, **93**, 745):

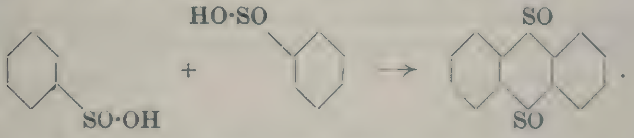
$$\begin{cases} C_6H_5{\cdot}SO{\cdot}Cl + C_6H_5{\cdot}SO_2H \longrightarrow C_6H_5{\cdot}SO{\cdot}C_6H_4{\cdot}SO_2H \\ C_6H_5{\cdot}SO{\cdot}C_6H_4{\cdot}SO_2H + C_6H_5{\cdot}SOCl \longrightarrow C_6H_5{\cdot}S(C_6H_4{\cdot}SO_2H)_2Cl, \end{cases}$$

and so on.

As a matter of fact, definite evidence of the production of sulphonium derivatives has not been obtained, but both of the other reactions appear to take place, the one or the other predominating according to the manner of substitution in the sulphinic acid used. Thus, from the action of heat on benzenesulphinyl chloride, a quantity of diphenyl disulphide and the white, insoluble compound mentioned above was formed, whilst *p*-toluenesulphinyl chloride yielded under similar conditions a mixture of di-*p*-tolyl disulphoxide and a small amount of di-*p*-tolyl-α-disulphone.

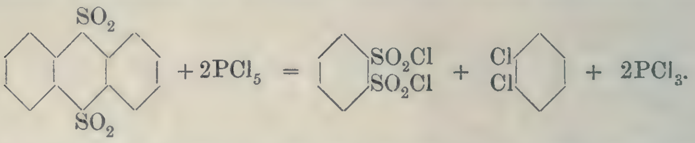
On the other hand, benzenesulphinic, *o*-toluenesulphinic, and α-naphthalenesulphinic acids reacted in the presence of concentrated sulphuric acid to form varying amounts of the insoluble products, together with disulphoxides. As much as 50 per cent. yields of the insoluble compound were obtained from benzenesulphinic acid, but only about 20 per cent. of the two other acids was converted to the corresponding insoluble derivative. Finally, *p*-toluenesulphinic, *p*-ethoxyphenylsulphinic, β-naphthalenesulphinic, and *o*-carboxybenzenesulphinic acids gave no "insoluble" product whatever, but usually furnished small amounts of disulphoxides.

Of these various compounds, the white, insoluble substances, which in the first place attracted attention to this decomposition, are perhaps the most interesting. Since these were not α-disulphones, it appeared probable that they had been formed by means of the condensation (ii) (*a*) referred to above, but from their insolubility in sodium hydroxide solutions it did not seem likely that any free sulphinic acid group was present in their molecules. Accordingly, the possibility of the remaining sulphinyl radicle having entered into the reaction had to be considered, and at first sight it appeared that derivatives of diphenylene *o*-disulphide had been formed:

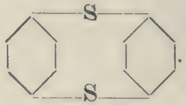


It soon became evident, however, from both physical and chemical properties of the products under investigation that they were not derived from ordinary diphenylene *o*-disulphide, and attention was next paid to a statement by Genvresse (*Bull. Soc. chim.*, 1896, [iii], **15**, 421, 1038; 1898, [iii], **17**, 599) that in the usual preparation of diphenylene *o*-disulphide large quantities of insoluble by-products were formed, and that under suitable conditions as much as 80 per cent. yields of an insoluble compound isomeric with diphenylene *o*-disulphide could be obtained from benzene, sulphur, and aluminium chloride. Genvresse suggested at the time that these compounds were para-condensation products, and that ordinary diphenylene disulphides contained meta-disulphide ring systems.

Recently, however, Deuss (*Ber.*, 1908, **41**, 2329) has established the constitution of diphenylene disulphide as an ortho-ring system by heating diphenylene disulphone, $C_6H_4[SO_2]_2C_6H_4$, with phosphorus pentachloride, when a mixture of *o*-dichlorobenzene and benzene-*o*-disulphonyl chloride was obtained according to the equation:



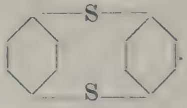
On treating the insoluble product derived from benzenesulphinic acid according to Deuss' directions, the author has obtained solid *p*-dichlorobenzene and benzene-*p*-disulphonyl chloride in sufficient amount for definite characterisation. It therefore appears that the compounds now being described are analogous to diphenylene *o*-disulphide, but are condensed into a ring system by means of their para-atoms:



A close comparison of the properties of these compounds with those described by Genvresse (*loc. cit.*) left no doubt that they were identical therewith; for example, the colour of their solutions in concentrated sulphuric acid is similar, but differs from that of the ortho-disulphides, whilst on oxidation a disulphone resulted identical in properties with that obtained by that author. Unfortunately, the compound from benzenesulphinic acid, which corresponds with a dioxide of Genvresse's isomeric compound, could not be reduced to the latter substance, owing probably to a simultaneous rupture of the ring system.

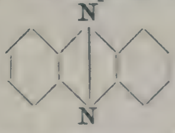
The proof of the orientation of these substances is strikingly supported by the fact that not a trace of the corresponding insoluble product could be obtained from either *p*-toluenesulphinic, *p*-ethoxyphenylsulphinic, or *β*-naphthalenesulphinic acids, the positions para- to the sulphinyl group being occupied in these instances by other radicles.

The author has, however, not succeeded in deciding whether these products are really analogous to diphenylene *o*-disulphide or whether they consist of an indefinitely prolonged series of $\cdot S \cdot C_6H_4 \cdot S \cdot$ groups united in para-positions. The latter alternative might be thought possible in view of their insolubility in practically all organic solvents, of their high melting points, and of their not too well-defined crystalline structure, but, on the other hand, para-substituted compounds usually melt higher and are less soluble than the corresponding ortho-derivatives, and, again, their general stability and the formation on oxidation of disulphones similar to diphenylene disulphone lend colour to the opinion that they are derived from the simple ring system:



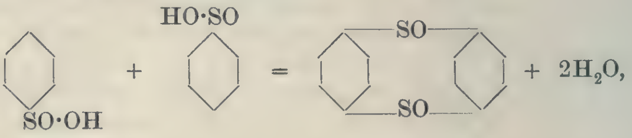
A determination of molecular weight, which would have definitely established the point, was unfortunately quite out of the question, owing to the exceedingly slight solubility or volatility of any of the compounds.

There is, however, little reason to suppose that a para-ring system as depicted above would be less stable, although less familiar, than the usual six-membered ring, for since it is generally conceded that the para-benzenoid atoms are almost as closely related in space as the ortho-atoms, the above ring system will partake much more nearly of the nature of a six-membered than of the ten-membered heterocyclic chain which at first sight it appears to be.

Before describing the experimental part of this investigation, it will be well to discuss the mechanism of the condensations which take place in diphenylene disulphide syntheses, and especially the non-appearance from sulphinic acids of any ortho-ring products. Speaking in general terms, the numerous syntheses of heterocyclic ring systems which have been worked out do not permit of any choice of orientation on the part of the molecules concerned. Thus, in the case of phenazine, the nitrogen atoms in which are situated similarly to the sulphur in diphenylene disulphide, derivatives of the system  result from *o*-phenylenediamine either by oxidation in presence of phenols (Ris, *Ber.*, 1886, **19**, 2207), or by condensation with catechol or derivatives of *o*-quinones (Hinsberg, *Annalen*, 1896, **292**, 258), but the oxidation of aniline itself leads not to phenazine, but to the "aniline-black" dyes, in which a number of benzene nuclei are united by means of nitrogen atoms each in a para-position with respect to the next.

It seems probable that similar influences determine the course of ring formation from sulphinic acids and mercaptans; moreover, the preference for para-condensation is emphasised in the case of sulphur compounds by the fact that, *ceteris paribus*, in the condensation of sulphinic acids or sulphoxides with phenolic ethers (Smiles and Le Rossignol, *loc. cit.*) para-substituted products predominate over ortho, the latter, indeed, being frequently not formed at all.

Again, all the synthetic methods for the preparation of diphenylene *o*-disulphides involve much loss of product owing to the formation of insoluble compounds, and it appears to the author that in most of these syntheses the formation of the disulphide is due to a secondary reaction, and may be ascribed to the fact that the starting materials are derivatives of phenyl mercaptan rather than of the more oxidised benzenesulphinic acid. The condensation of sulphinic acids is explained readily by the equation:



and it is probable that the underlying cause of all the earlier diphenylene disulphide syntheses is the production of temporary hydroxylic sulphur derivatives of the type $C_6H_5·S·OH$, rather than the simultaneous removal of a hydrogen atom from a mercaptan group and from a benzene nucleus by means of extraneous oxygen (compare Davis and Smiles, this vol., p. 1292).

Thus the chief methods extant for the synthesis of diphenylene *o*-disulphides are as follows:

(*a*) Action of sulphur on benzene in presence of aluminium chloride (Stenhouse, *Annalen*, 1869, **149**, 250; Krafft and Lyons, *Ber.*, 1896, **29**, 436).

(*b*) Action of aluminium chloride on mercaptans or disulphides (Deuss, *Rec. trav. chim.*, 1908, **27**, 145; 1909, **28**, 136).

(*c*) Action of hot concentrated sulphuric acid on mercaptans, disulphides, or disulphoxides (Fries and Volk, *Ber.*, 1909, **42**, 1170).

These reactions have been explained by the transitory formation of various oxidation and reduction products or by temporary isomerisation of the compounds involved, but it is evident that a simpler and more comprehensive explanation of the whole series results from the hypothesis that derivatives of sulphoxylic acids are first produced, as has been assumed by Davis and Smiles (*loc. cit.*) in the formation of thioxanthones, and by Hinsberg (*Ber.*, 1903, **36**, 109) in the formation of hydroxydiphenyl sulphide from benzenesulphinic acid and phenol.

The process is thus similar to the condensation of the sulphinic acids, and differs only in that, whilst in the latter case no ortho-condensation occurs, in the former instance derivatives of diphenylene *o*-disulphide are formed in varying, but subsidiary, proportions.

It should be mentioned here that phenyl mercaptan itself, on being kept for some hours in concentrated sulphuric acid at the ordinary temperature, was converted to a mixture of a small amount of diphenylene *o*-disulphide and about 70 or 80 per cent. of diphenylene *p*-disulphide.

The decomposition of disulphoxides in cold concentrated sulphuric acid is at present under investigation.

EXPERIMENTAL.

Action of Heat on Benzene- and p-*Toluene-sulphinyl Chlorides.*

(*a*) Five grams of benzenesulphinic acid were converted to the chloride by solution in ether and treatment with the theoretical quantity of thionyl chloride. It is found that this method yields a much cleaner product than the course formerly pursued of allowing excess of thionyl chloride to act on the undissolved acid in the cold. The ether was subsequently evaporated, and the residue heated on the water-bath for about an hour, when abundant evolution of hydrogen chloride took place. At the end of this period, the semi-solid product was extracted several times with boiling alcohol, after which the colourless, insoluble residue, which could not be crystallised from even such high boiling solvents as nitrobenzene or aniline, was dried at 130° and then analysed:

0·1023 gave 0·2186 CO_2 and 0·0321 H_2O. C=58·26; H=3·49.

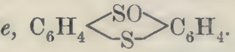
$C_{12}H_8O_2S_2$ requires C=58·07; H=3·23 per cent.

The alcoholic extract was found to contain a smaller quantity of diphenyl disulphide, melting at 59°, and identified with that substance by the mixed melting-point method.

(*b*) Two equal portions of benzenesulphinic acid were taken; one was converted into the acid chloride, and then heated with the other for some hours in boiling chloroform solution. As in the first instance, a large amount of *diphenylene* p-*disulphoxide*, together with a smaller amount of diphenyl disulphide, was obtained.

(*c*) Equal weights of benzenesulphinyl chloride and *p*-toluenesulphinic acid were heated in boiling chloroform for some time. After the evaporation of the chloroform, the product, which was very dark coloured, was first extracted with light petroleum, from which on evaporation a pale yellow oil was obtained, which was not closely examined, but appeared to be phenyl-*p*-tolyl disulphide (Otto and Rössing, *Ber.*, 1886, **19**, 3133). The residue was boiled with alcohol several times to remove tarry by-products, and an insoluble powder was thus formed, which again gave analytical numbers corresponding with diphenylene *p*-disulphoxide.

(*d*) Five grams of benzenesulphinic acid were heated for an hour with an amount of thionyl chloride in slight excess of that necessary for complete conversion to the acid chloride. The usual evolution of hydrogen chloride occurred, and the residue was extracted with boiling light petroleum, which removed a small amount of diphenyl disulphide, and then with boiling toluene, from which there separated a quantity of a white, crystalline substance, melting and decomposing at 180°. This proved to be a *monoxide* of *diphenylene* p-*disulphide*,



$C_6H_4{<}\substack{SO \\ S}{>}C_6H_4$.

0·1161 gave 0·2673 CO_2 and 0·0398 H_2O. $C=62·77$; $H=3·80$.
0·1192 „ 0·2712 CO_2 „ 0·0420 H_2O. $C=62·04$; $H=3·91$.
$C_{12}H_8OS_2$ requires $C=62·07$; $H=3·45$ per cent.

For comparison with this compound a sample of the monoxide of diphenylene *o*-disulphide was prepared from diphenylene *o*-disulphide by the method used by Fries and Volk (*loc. cit.*) in the preparation of the monoxide of ditolylene *o*-disulphide from ditolylene *o*-disulphide. Two grams of synthetic diphenylene *o*-disulphide, melting at 159°, were dissolved in glacial acetic acid, and dilute nitric acid (1 : 5) was added until a turbidity appeared. The solution was set aside for twenty-four hours at the ordinary temperature, and then poured into water. The precipitate was collected and crystallised from alcohol, when it formed colourless, glistening prisms, readily soluble in glacial acetic acid, benzene, or toluene, more sparingly so in alcohol, and melting at 148°:

0·1150 gave 0·2607 CO_2 and 0·0369 H_2O. $C=61·81$; $H=3·57$.
$C_{12}H_8OS_2$ requires $C=62·07$; $H=3·45$ per cent.

(*e*) On similarly heating 5 grams of *p*-toluenesulphinyl chloride in boiling chloroform, much tarry matter was produced, and, after evaporation of the chloroform, extraction with light petroleum yielded a white, crystalline substance, which melted at 74—76°, and appeared from its other properties to be di-*p*-tolyl disulphoxide. (Found, $C=61·06$; $H=6·34$. Calc., $C=60·43$; $H=6·04$ per cent.)

The residue was decolorised by repeated boiling with alcohol, and was found to crystallise from boiling toluene in small prisms, which melted at 210—212° (di-*p*-tolyl α-disulphone melts at 212°: Kohler and MacDonald, *Amer. Chem. J.*, 1899, **22**, 219; 221°: Hilditch, Trans., 1908, **93**, 1524). (Found, $C=53·20$; $H=4·17$; $C=54·22$; $H=5·49$. Calc., $C=54·20$; $H=4·52$ per cent.)

No trace of diphenylene *p*-disulphide derivatives was observed, and it would appear that, the para-position being already occupied by a methyl group, the reaction had taken the alternative course (i) referred to on p. 2580, in the presence of a certain amount of free sulphinic acid which must be assumed to have been regenerated:

$$\left\{\begin{array}{l} R{\cdot}SOCl + R{\cdot}SO_2H \longrightarrow R{\cdot}SO{\cdot}SO_2{\cdot}R \text{ (intermediate product)} \\ \quad 2R{\cdot}SO{\cdot}SO_2{\cdot}R \longrightarrow R{\cdot}SO{\cdot}SO{\cdot}R + R{\cdot}SO_2{\cdot}SO_2{\cdot}R. \end{array}\right.$$

Action of Cold Concentrated Sulphuric Acid on Benzenesulphinic Acid.

(*a*) Two grams of benzenesulphinic acid were converted to the chloride and poured into cold concentrated sulphuric acid. Hydrogen chloride was immediately disengaged in abundance throughout the solution in the form of minute bubbles, and after half an hour at the ordinary temperature, the reaction mixture was poured on crushed ice. The solid product was separated and boiled with alcohol, thus removing a small amount of diphenyl disulphoxide, which melted at 45°. The residue (diphenylene *p*-disulphoxide) was dried at 130° and analysed. (Found, $C=58{\cdot}22$; $H=3{\cdot}35$. Calc., $C=58{\cdot}07$; $H=3{\cdot}23$ per cent.)

(*b*) Ten grams of benzenesulphinic acid were left in solution in excess of cold concentrated sulphuric acid. The mixture, which was at first colourless, gradually turned purple, and was eventually of an almost black hue. On pouring into a large bulk of cold water, the colour entirely disappeared, and a granular, cream-coloured, solid product separated, and was collected and dried on a porous tile.

The whole was then boiled with alcohol under reflux for a time and again filtered; from the alcoholic filtrates about half a gram of diphenyl disulphoxide was obtained, which crystallised from light petroleum in characteristic, wax-like crystals, melting at 46°. (Found, $C=57{\cdot}00$; $H=4{\cdot}20$. Calc., $C=57{\cdot}60$; $H=4{\cdot}00$ per cent.)

The insoluble part of the product, when boiled for some time with alcohol, lost its crystalline appearance, and swelled up to a viscid, indiarubber-like mass. After removing the alcohol, however, the substance quickly became brittle again, and appeared gradually to break up into a microcrystalline powder on long keeping. This behaviour was also noticed with all the previously-described preparations of diphenylene *p*-disulphoxide, and also with the substituted derivatives subsequently mentioned.

The substance, which was then almost pure, was further submitted to two different methods of purification.

(i) A portion was boiled with toluene under reflux for some time, and was then collected and dried at 130° for some hours to remove adsorbed solvent and moisture, which was otherwise retained remarkably firmly. Diphenylene *p*-disulphoxide, as thus prepared, is a cream-coloured powder, practically insoluble in all the organic solvents tried (even in boiling nitrobenzene or aniline), but dissolving with a greenish-black colour in concentrated sulphuric acid. It commenced to soften and decompose without actually melting at 305°:

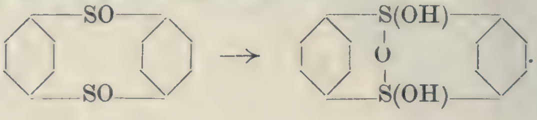
0·1035 gave 0·2194 CO_2 and 0·0298 H_2O. C=57·81; H=3·17.
$C_{12}H_8O_2S_2$ requires C=58·07; H=3·23 per cent.

(ii) The remainder of the preparation was boiled with water for two hours, and then collected and dried at 130° as above:

0·1353 gave 0·2685 CO_2 and 0·0485 H_2O. C=54·12; H=3·98.
0·1292 „ 0·2540 CO_2 „ 0·0401 H_2O. C=53·60; H=3·45.
$C_{12}H_8O_2S_2,H_2O$ requires C=54·13; H=3·76 per cent.

An attempt was made to remove this molecule of water by prolonged boiling with xylene, but a subsequent analysis showed that the composition of the product had not been altered. (Found, C=53·34; H=3·53.)

Water thus firmly attached is inconsistent with the presence of water of crystallisation, and it can only be surmised that some such hydrate formation as the following had taken place:



Oxidation of Diphenylene p-*Disulphoxide.*

Two grams of diphenylene *p*-disulphoxide were boiled for eight hours with a slight excess of anhydrous chromic acid in glacial acetic acid; oxidation ensued, and the hot reaction mixture was filtered, and the residue washed with boiling water until all traces of green chromium salts were removed, and then with boiling alcohol; an amorphous, white powder, which neither melted nor changed in appearance below 350°, was left. A sample dried in a vacuum desiccator was analysed:

0·0994 gave 0·1693 CO_2 and 0·0362 H_2O. C=46·45; H=4·05.
0·1380 „ 0·2343 CO_2 „ 0·0422 H_2O. C=46·30; H=3·40.
$C_{12}H_8O_4S_2,2H_2O$ requires C=45·57; H=3·80 per cent.

Reduction of Diphenylene p-*Disulphoxide.*

(*a*) Two grams of hydrated dioxide were heated for eight hours with 5 grams of sulphur at 150°; this process reduces the ortho-disulphoxide to the corresponding disulphide (Krafft and Lyons, *loc. cit.*), but on removal of excess of sulphur by means of carbon disulphide, the para-disulphoxide was found to have been unattacked.

(*b*) Three grams of the dioxide were heated under pressure at 160—180° with 1 gram of red phosphorus and 10 c.c. of hydriodic acid (D 1·7). Considerable pressure was generated, and the product was poured into water and extracted with benzene. A large proportion of insoluble matter was removed by filtration of the whole of the liquid, and the benzene layer was then dried and evaporated. It yielded a small amount of an oil, which soon crystallised, and, when purified by light petroleum, melted at 61°; analysis confirmed the supposition that this was diphenyl disulphide. (Found, C=66·01; H=5·01. Calc., C=66·06; H=4·60 per cent.)

An attempt made to purify the insoluble product, which was assumed to be diphenylene *p*-disulphide, by sublimation, led to the evolution of iodine vapours, and further experiments showed that the substance contained chemically bound iodine in quantity. Analysis proved that one atom of iodine was present in each diphenylene *p*-disulphide residue, but as the compound was not the desired parent substance it was not further studied; it is probably either an iododiphenylene *p*-disulphide or else a compound of the type $HS{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_4I$, formed by rupture of the para-ring system:

0·1800 gave 0·2750 CO_2 and 0·0516 H_2O. C=41·68; H=3·18.

$C_{12}H_7S_2I$ requires C=42·11; H=2·05 per cent.
$C_{12}H_9S_2I$,, C=41·86; H=2·62 ,,

Proof of the Constitution of Diphenylene p-*Disulphoxide.*

Six grams of the disulphoxide were ground in a mortar with 30 grams of phosphorus pentachloride, and heated in sealed tubes at 220° for six hours. The contents of the tubes were poured on ice, and subsequently extracted with ether; this extract was dried, the ether evaporated, and the residue distilled in a current of steam. The aqueous distillate contained an oil which quickly solidified to a mass of white needles, melting at 53°, and possessing the characteristic odour of *p*-dichlorobenzene. (Found, C=48·60; H=2·25. Calc., C=48·98; H=2·71 per cent.)

Since both *o*- and *m*-dichlorobenzene are liquids, the identity of the product was considered to be satisfactorily established.

The non-volatile portion of the product was extracted with ether and shaken with dilute sodium hydroxide; on evaporation of the dried ethereal solution, wax-like and not very well-defined crystals separated, melting at 131—133°; benzene-*o*-disulphonyl chloride melts at 105°; the *m*-compound at 63°; and the *p*-compound at 132°. (Found, C=26·70; H=1·26. Calc., C=26·18; H=1·46 per cent.)

The compound was further characterised by conversion into the sparingly soluble diamide, which formed small, hard prisms, and melted at 295°. The ortho-compound melts at 233°, the meta at 228°, and the para at 288°. (Found, C=29·92; H=3·89. Calc., C=30·51; H=3·39 per cent.)

Condensation of Phenyl Mercaptan in Cold Concentrated Sulphuric Acid.

Five grams of phenyl mercaptan were dissolved in concentrated sulphuric acid at the ordinary temperature, and the mixture vigorously shaken to dissolve the crystalline cake of diphenyl disulphide, which rapidly formed. After twenty-four hours, the deep purple-black reaction mixture was poured into a large bulk of cold water, the precipitate collected, dried, and extracted successively with boiling light petroleum and with hot alcohol. The absence of any solid on evaporation of the former solvent proved that no disulphide was left unattacked, whilst from the alcoholic filtrates a quantity of colourless, crystalline material was recovered, which, after further purification from alcohol, melted at 156—159°. A sample mixed with some pure diphenylene *o*-disulphide possessed the same melting point. About a gram of diphenylene *o*-disulphide, dissolving in concentrated sulphuric acid to a characteristic deep purple solution, was thus obtained. (Found, $C = 66{\cdot}66$; $H = 4{\cdot}54$. Calc., $C = 66{\cdot}67$; $H = 3{\cdot}70$ per cent.)

About 3 grams of a cream-coloured, amorphous powder, insoluble in boiling alcohol, were left from the above extraction, and this was boiled with acetic acid for an hour, collected, and dried at 130°. (Found, $C = 67{\cdot}04$; $H = 3{\cdot}88$. Calc., $C = 66{\cdot}67$; $H = 3{\cdot}70$ per cent.)

Genvresse (*loc. cit.*) states that diphenylene *p*-disulphide can be purified by sublimation; the sample under consideration was submitted to purification by this means, but did not sublime sufficiently readily for any quantity of the purified substance to be so isolated; enough was obtained, however, in minute, white needles for a determination of the melting point; the compound melted and decomposed at 290—295° (295°, Genvresse). Its solution in concentrated sulphuric acid was of a greenish-black hue.

Condensation of Other Aromatic Sulphinic Acids in Cold Concentrated Sulphuric Acid.

(*a*) p-*Toluenesulphinic Acid.*—The sulphinyl chloride on solution in sulphuric acid, evolved hydrogen chloride copiously, and gave a greenish-brown solution, which ultimately became deep purple. On pouring into cold water, no *p*-disulphide compound was obtained, and only a very small amount of disulphoxide, which melted at 76°.

A similar result was obtained from the condensation of the free acid.

(*b*) p-*Phenetolesulphinic Acid.*—The acid was dissolved in sulphuric acid in the usual manner, and the purple reaction mixture poured into water after a considerable time. The only insoluble product was a quantity of di-*p*-phenetole disulphoxide, which melted at 139° (a sample of the disulphoxide prepared in the usual way from *p*-phenetolesulphinic acid melted at the same temperature).

(*c*) *β-Naphthalenesulphinic Acid.*—The condensation was conducted as usual; the products of the reaction were all soluble in cold dilute acid, the solution being very deeply coloured. Neither derivatives of a *p*-disulphide nor any disulphoxide could be detected.

(*d*) *o-Toluenesulphinic Acid.*—On separation of the products of condensation in sulphuric acid of 5 grams of *o*-toluenesulphinic acid, it was found that rather more disulphoxide derivative had been produced than in the other cases. The di-*o*-tolyl disulphoxide crystallised from acetone in short, colourless prisms, melting at 97—98°. (Found, C = 60·09; H = 5·06. Calc., C = 60·45; H = 5·04 per cent.)

On the other hand, only about 20 per cent. of the sulphinic acid was converted into *p*-disulphide derivative in this instance; the *ditolylene* p-*disulphoxide* was a soft, colourless, insoluble powder, which softened, without actually melting, at 280°:

0·0909 gave 0·2004 CO_2 and 0·0375 H_2O. C = 60·12; H = 4·58.

$C_{14}H_{12}O_2S_2$ requires C = 60·87; H = 4·35 per cent.

(*e*) *α-Naphthalenesulphinic Acid.*—The amount of di-α-naphthyl disulphoxide obtained from the condensation was very small; it melted at 104°. A tolerably large proportion of insoluble matter resulted, but was contaminated by the presence of traces of dark-coloured products, even after prolonged boiling with various solvents. The probably still somewhat impure *dinaphthylene* p-*disulphoxide* finally analysed softened at 275—280°, and commenced to char at a rather higher temperature:

0·1902 gave 0·4760 CO_2 and 0·0730 H_2O. C = 68·26; H = 4·26.

$C_{20}H_{12}O_2S_2$ requires C = 68·98; H = 3·45 per cent.

(*f*) *o-Carboxybenzenesulphinic Acid.*—A sample of this acid was also submitted to the condensation in concentrated sulphuric acid. The dried product of the reaction was completely soluble in hot alcohol, no *p*-disulphide compounds having therefore been produced. From the alcoholic solution, pale yellow crystals of *di-o-carboxyphenyl disulphoxide*, melting at 228°, separated; the total amount of this product corresponded with about 10 per cent. of the original sulphinic acid employed:

0·1546 gave 0·2808 CO_2 and 0·0444 H_2O. C = 49·52; H = 3·20.

$C_{14}H_{10}O_6S_2$ requires C = 49·71; H = 2·96 per cent.

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CCLXV.—4-β-*Aminoethylglyoxaline* (β-*Iminazolylethylamine*) *and the other Active Principles of Ergot*.*

By GEORGE BARGER and HENRY HALLETT DALE.

FOR many years ergot has been notorious among drugs on account of the ignorance and division of opinion concerning the nature of its active principles. The problem had, indeed, approached solution in 1875, with Tanret's discovery of ergotinine and Buchheim's suggestion that ergot owes its activity to decomposition products of proteins produced by putrefaction. This discovery and suggestion were largely obscured by the work of subsequent investigators, which resulted rather in the physiological characterisation of impure products (sphacelinic acid, sphacelotoxin, etc.) than in chemical isolation of active principles.

Of late years, however, a considerable measure of agreement has been reached. The alkaloid ergotoxine (Barger and Carr) was also found by Kraft, who named it hydroergotinine, and the formulæ assigned to ergotinine and ergotoxine (Trans., 1907, **91**, 337) have been confirmed by Tanret and by Kraft respectively. There is also a consensus of opinion regarding the effect of ergotoxine on the blood-vessels and uterus, and its activity in producing gangrene.

Thus ergot, in common with many drugs, contains a complex physiologically active alkaloid. In addition, however, there are present in ergot a number of simpler bases, derived from amino-acids by the elimination of carbon dioxide. Such bases are generally formed in putrefaction. Ergot, as a fungus, is more closely related to bacteria than to the higher plants, from which all other important vegetable drugs are derived. Thus the peculiar nature of these active principles of ergot is due to its peculiar systematic position in the vegetable kingdom.

Putrefaction bases were first isolated from ergot by Rieländer (*Sitzungsber. Ges. Naturw. Marburg*, August 5th, 1908), who found putrescine and cadaverine, which only have a feeble physiological action. The first markedly active base of this class, *p*-hydroxyphenylethylamine, was isolated from ergot by ourselves (Barger and Dale, *Proc. Physiol. Soc.*, May 15th, 1909, in *J. Physiol.*, 1909, **38**, lxxvii; Barger, Trans., 1909, **95**, 1123). It is formed from tyrosine during putrefaction, but appears to be present also in fresh ergot. It is the chief pressor constituent of most aqueous ergot extracts, but does not produce contraction of the isolated uterus of the non-pregnant cat. In addition, we showed that *iso*-

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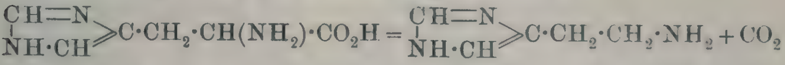
* A preliminary note on this subject was read at the meeting of May 26th, 1910.

amylamine (from leucine) is probably present in ergot, but in such proportion that it makes no significant contribution to the physiological action.

After the isolation of *p*-hydroxyphenylethylamine, there still remained unaccounted for the powerful action of certain aqueous ergot extracts in producing contraction of the isolated uterus, even of the non-pregnant cat, as observed by Kehrer. Since it was found quite impossible to remove the active substance from aqueous solution by means of organic solvents, a precipitation method had to be employed, and the ergot extract was subjected to the process worked out by Kutscher for the isolation of bases from meat extract. In this way we obtained a minute quantity of a crystalline picrate which gave Pauly's reaction with *p*-diazobenzenesulphonic acid, and exhibited in an intense degree the physiological action in question. It was not histidine picrate, for histidine was found to be inert; we therefore supposed it to be the picrate of 4-β-aminoethylglyoxaline (β-iminazolylethylamine), the base which would result from histidine by the loss of carbon dioxide:



$$\left.\begin{array}{l}\mathrm{CH{=}N}\\ \mathrm{NH{\cdot}CH}\end{array}\right>\mathrm{C{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H} = \left.\begin{array}{l}\mathrm{CH{=}N}\\ \mathrm{NH{\cdot}CH}\end{array}\right>\mathrm{C{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2} + \mathrm{CO_2}$$

and we confirmed this supposition by chemical and physiological comparison with a specimen of 4-β-aminoethylglyoxaline, very kindly sent us at our request by Dr. D. Ackermann, who a short time before had obtained this base by the putrefaction of histidine (*Zeitsch. physiol. Chem.*, 1910, **65**, 504). Simultaneously with ourselves, Kutscher (*Zentr. Physiol.*, 1910, **24**, 163) obtained a very active base from ergot, which he considered to be closely related to 4-β-aminoethylglyoxaline, although not identical with it, on account of a supposed difference in the physiological action of the two bases. It has, however, recently been shown that the differences in physiological action observed by Kutscher were presumably due to differences in the animals employed. One and the same base, whether from ergot or from histidine, can be made to produce the different effects described by Kutscher. On the other hand, the base from ergot and that from histidine, when tested successively on the same animal, gave identical effects. We have also analysed the picrate of the base from ergot, and have compared it and the picrolonate with the corresponding salts of 4-β-aminoethylglyoxaline (from histidine). As a result, we maintain our original conclusion (Proc., 1910, **26**, 128) that, contrary to Kutscher's view, the base in question is identical with 4-β-aminoethylglyoxaline. It is therefore the second active principle of ergot belonging to the class of putrefaction bases derived from amino-acids. Its physiological activity is very great. A marked contraction of the isolated uterus is produced by adding to the bath sufficient of the base to give a concentration of one part in 25 million parts of Ringer's solution; the effect of one part in 250 millions is often quite definite.

A third active principle of this class was quite recently found in ergot by Engeland and Kutscher (*Zentr. Physiol.*, 1910, **24**, 479). This is agmatine, $NH_2{\cdot}C(\colon NH){\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, discovered in herring roe by Kossel (*Zeitsch. physiol. Chem.*, 1910, **66**, 257). Its relation to arginine is analogous to that of 4-β-aminoethylglyoxaline to histidine, and it is said to have a similar action on the uterus.

EXPERIMENTAL.

Among the ergot preparations examined by Kehrer, the *ergotinum dialysatum* of Wernich is one of the most potent. We soon found, in making this extract on a small scale, that the activity of the substance which passed through the dialysing membrane finally exceeded that of the original extract, suggesting that more of the active principle was being formed by an enzyme or by bacteria. The active principle is, however, also present in perfectly fresh ergot, for the physiological effect was produced by a sample of ergot grown by ourselves and tested within half an hour of plucking. The effect was also produced to a smaller extent by commercial extracts of meat and of yeast, and this observation led to the adoption of Kutscher's method for the isolation of bases from meat extract. To 500 c.c. of commercial dialysed ergot extract, 500 c.c. of a 20 per cent. tannin solution were added, which quantity just ensured complete precipitation; next day the clear, supernatant liquid was decanted, and freed from tannin by the addition of barium hydroxide; after filtration, the excess of barium hydroxide was removed by dilute sulphuric acid, and the excess of sulphuric acid, together with the last traces of tannin, were precipitated by adding a suspension of freshly prepared lead hydroxide. After filtration, the liquid was concentrated to 300 c.c., and acidified with phosphoric acid. After adding excess of silver nitrate (400 c.c. of a 20 per cent. solution) and filtering, we found that the whole of the active substance was in the filtrate. To the latter, 150 c.c. more silver nitrate were added, when a drop of the solution at once produced a brown precipitate of silver oxide on mixing with barium hydroxide. The whole of the solution was then precipitated with barium hydroxide, until a sample, on filtration, gave only a slight opalescence with ammoniacal silver nitrate. This precipitate (silver II of Kutscher's method) in one preliminary experiment contained nearly the whole of the active substance, but afterwards it was found convenient to add at once to the filtrate from the first silver precipitate enough barium hydroxide for complete precipitation, thus collecting together silver precipitates II and III of Kutscher.

After washing, the silver precipitate was carefully suspended in very dilute sulphuric acid, and decomposed by hydrogen sulphide. The filtrate from the silver sulphide was freed from hydrogen sulphide, neutralised, and evaporated to dryness. The residue was extracted several times with hot ethyl alcohol, in which the active principle was found to be sparingly soluble; a large quantity of inert matter was left behind. The residue remaining on evaporating the alcoholic solution was dissolved in a little water, and a hot saturated aqueous solution of picric acid was added. After keeping for some days, a brown, imperfectly crystalline picrate was collected, washed, and recrystallised from water. This picrate was converted into a solution of the hydrochloride, which was very active physiologically, and gave an intense red coloration with sodium *p*-diazobenzenesulphonate (Pauly's reaction), suggesting a relationship to histidine. We had previously detected some activity in the crude histidine mother liquors obtained by hydrolysis of hæmoglobin with hydrochloric acid; histidine itself was found to be inactive, but it became so to a slight extent on heating to 300°. We were thus led to suppose that the picrate we had isolated was that of 4-β-aminoethylglyoxaline. After two crystallisations from water, the picrate from ergot formed dark yellow, rhombic plates, melting and decomposing at 234—235°. A specimen of the picrate sent us by Dr. D. Ackermann, when heated simultaneously in a tube attached to the same thermometer, also melted at 234—235°, and when recrystallised by evaporation of the solution in a desiccator, yielded rhombic plates exactly similar to those of the ergot base. Windaus and Vogt (*Ber.*, 1907, **40**, 3695) give the melting point as 239° on rapid heating, and the same crystalline form for a synthetic specimen of 4-β-aminoethylglyoxaline dipicrate. For analysis, the picrate was dried at 100° until constant:

0·0590 gave 0·0776 CO_2 and 0·0192 H_2O. C = 35·8; H = 3·6.

$C_5H_9N_3(C_6H_3O_7N_3)_2$ requires C = 35·8; H = 2·6 per cent.

We also prepared the very sparingly soluble picrolonate of the ergot base; it decomposed at 261° (Windaus and Vogt give 266° for 4-β-aminoethylglyoxaline dipicrolonate).

As the physiological action of the ergot base is also the same as that of 4-β-aminoethylglyoxaline, there is no room for doubt that the two bases are identical.

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CCLXVI.—*Viscosity and Association. Part I. Association of the Phenols.*

By FERDINAND BERNARD THOLE.

A STUDY of the literature on the subject of viscometry shows the existence of much evidence which indicates that association is accompanied by a considerable augmentation of viscosity (compare Dunstan and Thole, Trans., 1909, **95**, 1556).

On the other hand, in a paper published by Jones and Veazey (*Amer. Chem. J.*, 1907, **37**, 405), it was suggested that the depression of the degree of association of a liquid is accompanied by an increase in its viscosity. The increase in viscosity produced when alcohols are dissolved in water was explained by these authors as being due to a diminution of the association of each component, resulting in an increase in the number of non-associated molecules, and therefore of the available frictional surface. From a study of the viscosity-concentration curves for aqueous solutions of many inorganic salts, they also concluded that ions of large atomic volume, such as potassium, rubidium, and cæsium, give rise to the phenomenon of negative viscosity.

Since the relative degree of association of many phenols and their derivatives has been investigated by using a variety of physical methods, particularly cryoscopy, specific inductivity, and capillarity, it was considered of interest to compare the results obtained by viscometric methods with those determined by other physical methods.

Pinette (*Annalen*, 1888, **243**, 32) showed that the boiling points of the phenols are, in general, higher than those of their methyl ethers, and that ortho-substituted phenols boil at a lower temperature than their meta- and para-isomerides. The current ideas concerning association and steric hindrance are in accordance with these results, assuming the boiling points of similarly constituted compounds to vary in the same sense as the molecular weights.

Aston and Ramsay (Trans., 1894, **65**, 168), by measurement of the molecular surface energy of phenol, concluded that it was considerably associated.

Auwers (*Ber.*, 1895, **28**, 2878) carried out a very comprehensive series of cryoscopic investigations of the molecular weights of various phenols in naphthalene solution. He showed that whilst phenol is considerably associated, ortho-substituted phenols are practically unassociated, the association increasing to a maximum with the para-compounds. Meta-substituted phenols are associated to an intermediate degree, but approximate more nearly to the para-series. In the ortho-series, the aldehyde group has the greatest effect in inhibiting association; then, in order, follow the carbethoxyl, nitro-, halogen, and finally alkyl groups.

Speranski (*Zeitsch. physikal. Chem.*, 1903, **46**, 70) determined the vapour pressures of solid solutions of β-naphthol in naphthalene, and concluded that the former compound is associated.

Philip and Haynes (Trans., 1905, **87**, 998) measured the dielectric constants of phenol, its methyl and ethyl ethers, and of the cresols in benzene and in *m*-xylene solutions. Their results indicate that, whilst the ethers are unassociated, phenol and the cresols are distinctly associated, *o*-cresol to the least extent.

Hewitt and Winmill (Trans., 1907, **91**, 441), using the capillarity method of Ramsay and Shields, studied the association of a considerable number of substituted phenols and allied substances. Their results are included in table I, and show that the phenols in general are associated, the association being least in the ortho-series. Considerable depression of association is produced by the carbethoxyl, nitro-, and halogen groups, but alkyl groups only exert a slight influence. Benzyl alcohol was shown to be associated, but the introduction of phenyl groups inhibits this to such an extent that benzhydrol and triphenylcarbinol are practically unassociated. It appears uncertain whether substitution in the meta- or para-positions has the greater effect, the results on this point being indecisive. It seems to the author, however, that, although the capillarity method will show satisfactorily whether or no a substance is associated, little trust can be placed in figures indicating the actual degree of association, for in a mixture one is not entitled to assume that the constitution of the surface layer is typical of that of the bulk of the liquid, and associated liquids may fairly be regarded as mixtures of molecular aggregates and simple molecules

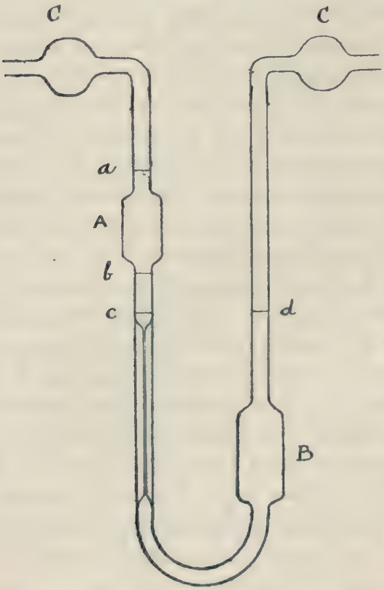
EXPERIMENTAL.

As the apparatus used has been considerably modified with a view to increased accuracy since it was previously described by the author (this vol., p. 1251), a somewhat detailed account of the viscometer and the accompanying fittings may be of interest.

The viscometer was of the original Ostwald type, but was provided with four etched marks instead of two. Guard tubes were also attached to the two limbs, and were provided with bulbs, which contained cotton wool moistened with the liquid under investigation. By adopting this precaution, volatile liquids, such as acetone and benzene, may be safely used as solvents. The dimensions of the viscometer may, of course, be varied, according to the quantity and nature of the liquid used. For the present research, the bulbs *A* and *B* contained approximately 3 and 5 c.c. of liquid respectively. The length of the capillary was 8 cm., and the diameter 0·025 cm.

Before use the viscometer was cleaned successively with hot chromic acid mixture, hot absolute alcohol, and boiling, filtered conductivity water. Finally, it was dried in a current of warm dust-free air. Every precaution is necessary to avoid the introduction of dust, as this will inevitably choke the capillary.

The clean, dry viscometer was suspended by means of a carrier provided with spring clips in a copper thermostat fitted with large windows front and back. In this bath were fixed a stirrer connected with a small hot-air motor, a standard thermometer, a Beckmann thermometer graduated to 0·01°, and a Lowry thermoregulator of the "spiral" pattern. The determinations were carried out in a laboratory allocated for the purpose, and the variation of temperature of the thermostat did not exceed 0·02°.



The liquid was filtered or, whenever possible, distilled into the viscometer, and after the apparatus had remained in the thermostat for ten minutes, the level of the liquid was adjusted to the marks *c* and *d*. Cotton wool contained in the guard tubes *cc* was moistened with the liquid, the tubes attached, the viscometer accurately adjusted to a vertical position by means of three plumb lines, and the time of flow of the liquid from *a* to *b* measured in the usual way. A stop watch, reading to 0·2 second, was used. Usually about seven observations, differing by not more than 0·5 second, were made, and the mean was taken.

The densities were determined in a Sprengel pyknometer of 5 c.c. capacity, and in the case of phenol and *p*-chlorophenol in a 10 c.c. specific gravity bottle. Each estimation was repeated until concordant results were obtained, and a correction was introduced for the weight of displaced air.

The constants of the instruments were determined from time to time, using conductivity water. The values adopted for the viscosity of water were those determined by Thorpe and Rodger.

For the two determinations at 130°, the ordinary thermostat was replaced by a large beaker filled with heavy petroleum and heated by a small burner. The temperature was regulated by hand, the maximum fluctuation being 0·2°.

The substances used in the research were carefully purified by repeated fractionation with a rod-and-disk column or by recrystallisation. In no case did the liquid used for the determination boil over a greater range than 0·2°. Unless otherwise stated, the fraction used boiled constantly. The source and method of purification of the materials is indicated below.

Phenol.—Kahlbaum's "synthetic" phenol. Fractionated three times.

Anisole.—The specimen used was obtained from a large quantity of the carefully dried ether.

Phenetole.—Purified in the same way as anisole.

Phenyl Acetate.—Prepared from synthetic phenol and acetic anhydride. The specimen was free from phenol and acetic acid.

Cresols.—Schuchardt's purest products, fractionated three times.

Tolyl Methyl Ethers.—Carefully dried and fractionated.

o-*Chlorophenol.*—Fractionated three times from a specimen supplied by Kahlbaum.

m-*Chlorophenol.*—Purified by freezing out and subsequent fractionation. The specimen boiled within 0·2°.

p-*Chlorophenol.*—Purified by freezing out and subsequent fractionation.

o-*Nitrophenol.*—Three times distilled in a current of steam, and finally recrystallised from absolute methyl alcohol.

m-*Nitrophenol.*—Twice recrystallised from pure benzene, and dried in a vacuum over paraffin wax.

p-*Nitrophenol.*—Freed from traces of the ortho-isomeride by means of a current of steam, twice recrystallised from dilute hydrochloric acid, and dried in a vacuum over potassium hydroxide.

Ethyl Salicylate.—Fractionated three times from a quantity of the pure ester.

Ethyl m-*Hydroxybenzoate.*—Twice recrystallised from pure benzene, and dried in a vacuum over paraffin wax.

Ethyl p-*Hydroxybenzoate.*—Twice recrystallised from absolute alcohol.

Salicylaldehyde.—Fractionated twice.

Benzyl Alcohol.—Prepared from re-distilled benzaldehyde by the Cannizzaro reaction, and fractionated three times. The specimen used boiled within 0·2°.

Benzyl Acetate.—Fractionated three times.

Benzyl Methyl Ether.—Prepared from pure benzyl chloride and methyl-alcoholic sodium methoxide. The specimen was free from halogen and from methyl alcohol.

Benzhydrol.—Prepared from re-distilled benzaldehyde and magnesium phenyl bromide, and crystallised several times from light petroleum.

Triphenylcarbinol.—Recrystallised from benzene.

α- and β-Naphthols.—Fractionated from Schuchardt's purest products.

Amyl Acetate.—A large quantity of Kahlbaum's purest product was twice fractionated. It boiled within 0·5°.

Ethyl Alcohol.—Kahlbaum's absolute alcohol was fractionally distilled over cleaned calcium turnings.

As the differences of viscosity are most marked in the case of the pure substances, the viscosities of all those which are liquid at 45° were measured at this temperature. Since some of the compounds it was desirable to investigate are solid at this temperature, solutions of these substances had to be used.

Some care had to be exercised in the choice of a solvent which would have the least dissociating effect and at the same time would readily dissolve the substances, which would have a low vapour tension (to minimise errors due to evaporation), and could easily be obtained in a fairly pure state. Amyl acetate was finally chosen as fulfilling these conditions most nearly.

The solutions used were of equimolecular strength, 1/100th of a gram-molecular weight of the substance being accurately weighed into a stoppered weighing bottle, and dissolved in 6 c.c. of amyl acetate, which was run in from a suitably graduated pipette.

In two instances (with ethyl *p*-hydroxybenzoate and triphenylcarbinol), it was found impossible to prepare solutions of this strength, and in these cases the viscosities of several solutions of lower concentration were determined, the value for the stronger solution being obtained by extrapolation. Although the accuracy of these results may not be of the same order as in the direct determinations, the qualitative nature of the results is not affected.

It has been shown (Dunstan and Wilson, Trans., 1907, **91**, 83; Getman, *Amer. Chem. J.*, 1903, **30**, 1077) that the value of the expression $\frac{\eta}{\text{Mol. vol.}} \times 10^6$ indicates to some extent the existence of association in a liquid. For each particular series of compounds, this quantity is approximately constant, and for non-associated liquids does not exceed 60. The values for hydroxylated liquids are, however, much higher, those for water, ethyl alcohol, and ethylene glycol being respectively 494, 193, and 2750, and the variation of the value of this expression is a very sensitive indication of association.

The values for each of the substances investigated is given in the tables, and affords, perhaps, the best means of comparing the results. It should be noted, however, that this value is affected to some extent by symmetry as well as by association. This is seen in the case of the tolyl methyl ethers, and more particularly in the case of benzyl methyl ether, where the value of $\frac{\eta}{\text{Mol. vol.}} \times 10^6$ is slightly higher than the mean figure for the unassociated ethers, probably owing to the comparatively long side-chain.

TABLE I.

The Pure Substances at 45°.

Substance.	Time of flow in seconds.	Density.	Viscosity.	$\frac{\eta}{\text{Mol. vol.}} \times 10^6$	Hewitt and Winmill's association constants.
Phenol	837·2	1·055	0·04036	453·0	1·3
Phenyl acetate.........	374·2	1·052	0·01799	136·0	—
Anisole....................	167·0	0·9707	0·007409	66·6	—
Phenetole...............	191·4	0·9427	0·008249	63·8	—
p-Chlorophenol	1044·8	1·260	0·06018	590·0	1·22
m-Chlorophenol	826·9	1·249	0·04722	459·0	1·49
o-Chlorophenol	406·7	1·210	0·02250	212·0	1·0
p-Cresol	1208·8	1·015	0·05607	527·0	1·62
m-Cresol	1091·3	1·014	0·05057	475·0	1·48
o-Cresol..................	742·7	1·027	0·03506	333·0	1·12
m-Tolyl methyl ether	200·6	0·9546	0·008753	68·5	—
o-Tolyl methyl ether	193·7	0·9589	0·008491	66·7	—
p-Tolyl methyl ether	185·8	0·9497	0·008064	62·8	—
o-Nitrophenol	433·5	1·183	0·02343	199·0	0·84
Ethyl salicylate	350·5	1·106	0·01772	118·0	0·9
Salicylaldehyde	320·1	1·141	0·01669	156·0	—
Benzyl alcohol.........	640·5	1·027	0·03008	286·0	1·66
Benzyl acetate.........	296·5	1·033	0·01399	96·3	—
Benzyl methyl ether	233·6	0·9624	0·01028	81·1	—
β-Naphthol (at 130°)	376·0	—	—	—	—
α-Naphthol (at 130°)	312·6	—	—	—	—

TABLE II.

Solutions in Amyl Acetate at 25°.

Substance.	Time of flow in seconds.	Density.	Viscosity.	$\frac{\eta}{\text{Mol. vol.}} \times 10^6$.
Amyl acetate	201·4	0·8659	0·008055	—
Phenol	267·1	0·8951	0·01105	105·0
Anisole............................	202·0	0·8856	0·008265	67·8
Phenyl acetate	223·3	0·9033	0·009319	61·9
Phenetole	209·6	0·8829	0·008550	61·4
p-Chlorophenol	295·9	0·9289	0·01270	91·8
m-Chlorophenol	290·3	0·9274	0·01244	89·8
o-Chlorophenol	281·1	0·9254	0·01202	86·5

TABLE II. (*continued*).

Solutions in Amyl Acetate at 25°.

Substance.	Time of flow in seconds.	Density.	Viscosity.	$\frac{\eta}{\text{Mol. vol.}} \times 10^6$.
p-Cresol	283·4	0·8931	0·01169	96·7
o-Cresol	281·3	0·8964	0·01165	96·7
m-Cresol	282·9	0·8928	0·01167	96·5
m-Tolyl methyl ether	214·9	0·8847	0·008784	63·7
o-Tolyl methyl ether	211·7	0·8853	0·008659	62·8
p-Tolyl methyl ether	210·6	0·8840	0·008602	62·3
p-Nitrophenol	358·5	0·9440	0 01564	106·0
m-Nitrophenol	331·1	0·9418	0·01449	98·2
o-Nitrophenol	242·9	0·9365	0·01051	70·8
*Ethyl *p*-hydroxybenzoate ...	—	0·931	0·0166	93·0
Ethyl *m*-hydroxybenzoate ..	370·9	0·9261	0·01587	88·6
Ethyl salicylate	246·3	0·9184	0·01045	57·6
Benzyl alcohol	250·6	0·8943	0·01035	85·7
Benzhydrol	351·4	0·9212	0·01496	74·9
*Triphenylcarbinol	—	0·97	0·0190	70·0
Benzyl methyl ether	207·8	0·8832	0·008479	61·4
Benzyl acetate..................	233·6	0·9023	0·009738	58·6
β-Naphthol	375·5	0·9210	0·01598	102·0
α-Naphthol	371·2	0·9031	0·01549	97·1

* By extrapolation.

TABLE III.

The Chlorophenols in Ethyl Alcohol at 25°.

Substance.	Time of flow in seconds.	Density.	Viscosity.	$\frac{\eta}{\text{Mol. vol.}} \times 10^6$.
Alcohol	309·2	0·7876	0·01125	—
p-Chlorophenol.........	364·0	0·8646	0·01454	97·8
o-Chlorophenol.........	364·2	0·8628	0·01452	97·5
m-Chlorophenol	363·7	0·8631	0·01450	97·4

Discussion of Results.

Table I.—The results in column 4 follow very closely those obtained by Auwers and by Hewitt and Winmill, with one exception. In two cases (the cresols and hydroxybenzoic esters), the latter authors found the order of increasing association to be ortho—meta—para, and in two other cases (the chloro- and nitro-phenols) to be ortho—para—meta, whereas Auwers in all cases found the order to be ortho—meta—para, the meta-compound approximating more nearly to the para-compound.

The viscosity results are in full agreement with those of the latter author, though it must be remembered that V. Meyer found the order of steric hindrance in the case of the esterification of substituted benzoic acids to be ortho—para—meta (*Ber.*, 1895, **28**, 1254).

That the order of the viscosity results is not merely due to the position of the substituent group in the benzene nucleus apart from its influence on the hydroxyl group is shown by the fact that the values for the tolyl methyl ethers do not fall in this order.

It will be noticed that the mean value of the expression $\frac{\eta}{\text{Mol. vol.}} \times 10^6$ for the ethers is 66, these compounds being practically unassociated. The value for benzene is 65 (Dunstan, *Zeitsch. physikal. Chem.*, 1905, **51**, 738).

In the case of benzyl methyl ether, the slightly higher value may be due to disturbance of the symmetry of the molecule by the comparatively long side-chain. Phenyl and benzyl acetates appear to be slightly associated, this being probably due to the slight residual affinity possessed by the carbonyl oxygen atom in the acetyl group.

For benzyl alcohol and all the phenols, $\frac{\eta}{\text{Mol. vol}} \times 10^6$ is marked higher, indicating considerable association. Ortho-substituted phenols appear to be less associated than phenol itself, presumably owing to the proximity of the substituent to the source of association, the carbethoxyl, aldehyde, nitro-, and halogen groups exercising very considerable influence. The marked effect of these groups has been pointed out by Auwers and by Hewitt and Winmill.

The results obtained by Auwers indicate that the aldehyde group has the greatest inhibiting influence, followed in order by the carbethoxyl, the nitro-, the halogen, and finally the alkyl groups. The viscosity results, while agreeing in the main with these, invert the order of the first two groups. No satisfactory explanation of this discrepancy is apparent.

It is noteworthy that in the first four cases the ortho-substituent contains an unsaturated nucleus, and it appears probable that the latent valency of this nucleus in some way attracts part of that of the hydroxyl group, thus lessening the tendency for association. This action is, of course, supplementary to the steric hindrance produced by the ortho-substituent by virtue of its proximity to the hydroxyl group.

This explanation is rendered still more probable by the fact that the aldehyde and carbethoxyl groups, which depress association most strongly, are known to be markedly unsaturated, whilst the methyl group, which exercises only a slight inhibitive influence, is practically saturated.

An interesting parallel is observed when the molecular refractivities of various substituted benzene derivatives are considered (Smiles, *Chemical Constitution and Physical Properties*, p. 298).

Substance.	$M_{(\alpha)}$ (obs.).	$M_{(\alpha)}$ (calc.).	Δ.	Δ due to substituent.
Phenylacetylene	34·46	33·53	+0·93	+1·31
Styrene	35·98	35·08	+0·90	+1·28
Benzaldehyde	31·77	31·01	+0·76	+1·14
Nitrobenzene	32·69	32·10	+0·59	+0·97
Benzonitrile	31·32	30·75	+0·57	+0·95
Aniline	30·27	29·72	+0·55	+0·93
Acetophenone	36·00	35·58	+0·42	+0·80
Methyl benzoate	37·55	37·23	+0·32	+0·70
Phenol	—	—	−0·07	+0·31
Iodobenzene	—	—	−0·24	+0·14
Bromobenzene	—	—	−0·31	+0·07
Chlorobenzene	—	—	−0·32	+0·06
Benzene	—	—	−0·38	—

The degree of disturbance of the benzene system increases with the increasing degree of unsaturation of the substituent. It has also been shown, from measurements of molecular magnetic rotation (Perkin, Trans., 1896, **69**, 1152), that the anomaly shown by dimethylaniline is diminished when the residual affinity of the basic group is satisfied by the addition of hydrochloric acid. A similar argument appears to explain the gradual decrease in the reactivity of the carbonyl group in the series acetone—ethyl acetate—acetic acid. In the first compound, where the carbonyl group is adjacent to two saturated methyl groups, it possesses a sufficient degree of unsaturation to combine with sodium hydrogen sulphite and with hydrogen cyanide. In ethyl acetate one of the adjacent groups is ethoxyl, the oxygen atom of which possesses a certain amount of latent affinity (compare the combination of ethyl ether with hydrogen chloride and with magnesium alkyl halides). This affinity exerts an attractive influence on part of the latent affinity of the carbonyl group, with the result that ethyl acetate will not combine with such a number of reagents as will acetone.

In acetic acid, the oxygen of the hydroxyl group possesses considerable residual affinity, part of which is united with that of the carbonyl group, which thus loses its characteristic additive properties, whilst the remainder produces association of the molecules.

Owing to the comparatively high temperature employed in working with the fused naphthols, accurate density measurements were not attainable, and only the time of flow (the chief factor in determining the viscosity) was measured. The results indicate clearly the influence of the second ring of the naphthalene nucleus in hindering the association of α-naphthol. V. Meyer observed a similar effect when measuring the velocities of esterification of 2-chloro-1-naphthoic acid and 3-chloro-2-naphthoic acid, the former compound esterifying very slowly (*Ber.*, 1895, **28**, 182).

Table II.—It should be pointed out that the results in column 4 have been obtained with solutions of an empirical concentration,

and are therefore comparable only among themselves, and not with the corresponding figures in table I.

It will be seen that the results in table I are exactly confirmed, and also that a further range of substances has been studied. In each case the phenols are associated, the ortho to the least, and the para to the greatest extent, the meta-compounds, as before, approximating more closely to the para-compounds. The gradual inhibition of the association of benzyl alcohol by the progressive replacement of the hydrogen atoms of the side-chain by phenyl groups is also clearly indicated. This, again, is in full agreement with surface energy results. Although the figures for triphenylcarbinol are obtained by extrapolation and therefore are not of the usual degree of accuracy, it is clear that this substance approximates to the ethers in its slight degree of association.

Ethyl salicylate and *o*-nitrophenol, again, show practically no signs of association.

A very striking point is the dissociating influence of the amyl acetate. This was specially chosen as a comparatively inert, non-dissociating solvent, but its effect on the associated solutes is most marked. The viscosities of the cresols in the pure state differ very considerably, but solution evidently breaks down the complexes to a large extent, and the viscosities of the solutions are almost identical. The dissociating influence is more marked in this case than in that of the other phenols, the cresol complexes being apparently more unstable than those of the other substituted phenols. If the difference between the values for $\frac{\eta}{\text{Mol. vol.}} \times 10^6$ found for ortho- and para-isomerides be taken as a measure of the relative stability of the complexes, this stability decreases in the order carbethoxyl—nitro—halogen—alkyl. The slight signs of association noticeable in the pure phenyl and benzyl acetates disappear in the amyl acetate solutions, and the substances appear to be completely dissociated.

Table III.—As it was observed that a comparatively non-dissociating solvent had such a marked disruptive effect on the molecular aggregates, it was considered of interest to determine the viscosities of solutions of a set of three isomerides in a dissociatng solvent. For this purpose, solutions of the chlorophenols in ethyl alcohol were chosen, and the results indicated that practically complete dissociation had resulted. Preliminary experiments with solutions of the chlorophenols in light petroleum (one of the least dissociating of ordinary solvents) showed that the dissociation produced was less than in the case of amyl acetate, and a detailed study of the effect of various solvents on associated substances is now being carried out.

Summary of Results.

(1) The results obtained by the viscometric method agree very closely with those derived from other physical constants, such as vapour pressure, dielectric constant, molecular surface energy, molecular refractivity, and molecular weight determined cryoscopically.

(2) Viscosity determinations, using $\frac{\eta}{\text{Mol. vol.}} \times 10^6$ as a criterion of association, show that phenols are associated, the ortho-compounds to the least, and the para-compounds to the greatest extent. The ethers are unassociated, but the acetates show slight association.

(3) The carbethoxyl, aldehyde, nitro-, and halogen groups exert a marked inhibitive influence on association. Alkyl groups only exert a slight influence. Since the degree of inhibition of association appears to be intimately connected with the degree of unsaturation of the substituent, it is suggested that the depression of association is partly due to some kind of attraction between the latent valency of the hydroxylic oxygen and the unsaturated substituent, the consequence being a diminution of the tendency to form complexes through the latent valency of the hydroxyl group. The same hypothesis explains the gradual disappearance of the characteristic reactivity of the carbonyl group in the series acetone—ethyl acetate —acetic acid.

(4) Solution in even a comparatively inert solvent, such as amyl acetate, produces considerable disruption of the molecular aggregates. In a dissociating solvent, such as ethyl alcohol, the dissociation is practically complete.

The author desires to express his sincere thanks to Dr. J. T. Hewitt and to Dr. A. E. Dunstan for the interest they have taken in the work, and to the Chemical Society for a grant which has covered the expense entailed.

EAST LONDON COLLEGE. EAST HAM TECHNICAL COLLEGE.

CCLXVII.—*Binary Mixtures of Some Liquefied Gases.*

By BERTRAM DILLON STEELE and L. S. BAGSTER.

THE work described in this paper was undertaken in the first place in connexion with the study of simple inorganic solvents.

Combination between solute and solvent is usually held to be a necessary antecedent to conduction, whilst the form of the vapour pressure-composition curve for mixtures of volatile substances is often accepted as evidence for or against combination in such solutions.

One of us (*Proc. Roy. Soc.*, 1904, **73**, 450) has found that mixtures of the halogen hydrides with hydrogen sulphide form solutions which do not conduct, whilst we have examined sulphur dioxide and hydrogen bromide, and found them to mix in all proportions, forming solutions which show but very slight conductivity. The hydrogen sulphide solutions are doubly interesting, owing to the analogy between hydrogen sulphide and water.

We therefore decided to examine the vapour pressure-composition curves of the solutions formed by sulphur dioxide and by hydrogen sulphide with the halogen hydrides. Hydrogen chloride solutions have not been systematically examined, owing to difficulties caused by the low boiling point of the hydrogen chloride, and to the absence of liquid air. We have, however, found from some rough experiments that sulphur dioxide at $-35°$ dissolves hydrogen chloride to form a solution approximately normal, and that all the hydride can be removed from such a solution by fractional distillation, and therefore no constant boiling mixture can be formed at this temperature. Judging from analogy, also, one would expect the curve obtained to be of a similar type to that given by sulphur dioxide and hydrogen bromide, which pair of liquids has been systematically examined.

Mixtures of hydrogen iodide and sulphur dioxide could not be formed, owing to the fact that these substances react in the gaseous state, depositing sulphur and iodine.

It will be convenient, first, to describe the apparatus used and the method of working, following this with an account of the results obtained. For the preparation of the various hydrides used, the methods described in the paper previously mentioned have been followed. The sulphur dioxide was obtained commercially in a steel cylinder, and fractionated before use. For the preparation of the liquid hydrogen sulphide and bromide, a mixture of solid carbon dioxide and ether was used as refrigerant, liquid ammonia being used to condense the sulphur dioxide and hydrogen iodide. In the actual experiments, liquid ammonia was used for the low temperature bath, constant temperatures from −35° to −75° being easily obtained by varying the pressure over the ammonia by means of a water pump.

Ammonia and hydrogen iodide boil at about the same temperature, but it was found that if the top of the vacuum vessel containing ammonia were left open to the air and not plugged with cotton wool, as is usual, the diminution in the partial pressure of the ammonia, brought about by air convection currents, was sufficient to lower the temperature to 10° or 15° below the boiling point of the ammonia under atmospheric pressure. The temperature thus obtained was sufficiently low to condense the hydrogen iodide, and as the carbon dioxide mixture froze the liquid in the condenser, the above method of cooling was adopted. If the temperature rose owing to heat given out by the condensing hydride, an air current occasionally blown through the ammonia by means of a foot-bellows sufficed to reduce it again.

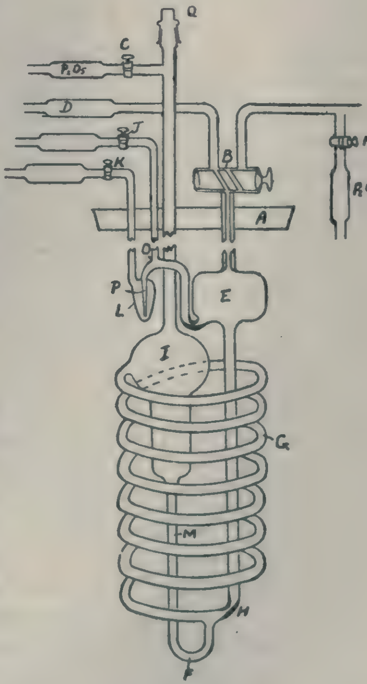
The difficulty of measuring the vapour pressure of substances, such as the halogen hydrides, which attack mercury was overcome by using the glass spiral manometer of Ladenburg and Lehmann (*Ber. Deut. physikal. Ges.*, 1906, **8**, 20), as modified by Johnson (*Zeitsch. physikal. Chem.*, 1908, **61**, 458).

It may be mentioned here that as the halogen hydrides are decomposed by organic matter, rubber tap grease was not used, being replaced by a mixture of pure paraffins. On account of the extremely hygroscopic nature of the halogen hydrides, every entrance to the apparatus by means of which moisture could gain access was protected by a phosphoric oxide tube, and as the oxide appeared to contain some impurity which slowly reacted with the halides, the tubes containing it were attached to the apparatus with taps interposed as shown in Fig. 1. The oxide was thus only exposed to the halides for short periods.

Fig. 1 shows the apparatus used. Glass was, of course, used for its construction, and all joints were sealed. The apparatus was fitted with a rubber cork *A*, selected to fit closely the mouth of an unsilvered, cylindrical Dewar flask. The various tubes were passed through holes in the cork, and sealed to the apparatus afterwards. In addition to the holes for the apparatus, the cork was bored to contain the thermometer, a glass tube for making connexion with a water pump for reducing the pressure over the ammonia, another tube closed by rubber tubing and a pinchcock for the admission of fresh ammonia, and a glass tube drawn to a capillary at its lower end, which reached to the bottom of the vacuum vessel, the top being also closed by rubber tubing and a pinchcock. The purpose of this tube will be explained presently.

Between the water pump and the vessel containing the ammonia was interposed a piece of rubber pressure tubing, which could be more or less closed by means of a screw clip. To obtain any desired temperature below the boiling point of the ammonia, the pump was set in action while a stream of air was admitted through the capillary. The ammonia boiled under the reduced pressure, and its temperature fell. The air stream served to prevent superheating and subsequent bumping, and also to stir the liquid and obtain a uniform temperature throughout the bath. When the temperature was near the desired point, the pressure tubing was partly closed by means of the screw clip, thus checking the rate of withdrawal of the ammonia vapour, and consequently the rate of evaporation, so lessening the heat absorption and fall of temperature. In a short time a state of equilibrium was reached, and by this means the temperature could be kept constant to 0·1° for half an hour. If it varied, a slight turn of the screw clip occasionally sufficed to adjust it again. It was possible to run for half an hour without adding fresh ammonia.

Fig. 1.



A normal pentane thermometer, reading to −115°, was used. It was not wholly immersed, and there was a large correction for the exposed portion of the stem, which correction is probably nearly correct at the lower temperatures, but may have an error of about a degree at the higher. As our object was to work at a constant temperature rather than to know its exact value, slight errors are in our case not important, as our vapour pressure-composition curves are constructed at constant temperature.

The construction of the actual apparatus will be apparent from Fig. 1. A description of the method of working should render the use of the various parts clear.

The temperature of the ammonia-bath was reduced to well below the boiling point of the liquid it was desired to use. The liquid previously condensed in another vessel was then distilled into the apparatus through *O* and the three-way tap *B*. The first few drops of liquid condensed collected in the bend *F*, after which all uncondensed gas travelled round the spiral *G* rather than force its way against the pressure of the liquid in *F*. By this means, thorough condensation was secured. The capacity of the apparatus was known at various points, so that mixtures of any desired strength could be made up approximately by distilling in the necessary volumes of each liquid. This was more necessary in changing the composition of a previous mixture than in preparing the first one, when the volumes of liquid distilled in could, of course, be measured. About 25 c.c. of liquid were necessary to fill the apparatus to the amount necessary for its correct working.

To ensure thorough mixing of the two liquids, a hydrogen generator was connected to *D*, and hydrogen passed through *E*. When the gas reached the point *H*, it broke into bubbles, which ran around the spiral *G*, carrying liquid with them into the bulb *I*, from whence the liquid flowed back through *M*, while the gas passed out at *C*. The hydrogen pressure was now applied at *C*, the taps *B*, *J*, and *K* having been closed. These taps were then carefully opened, when the liquid rose, filling the bulbs *E* and *L*, and on reaching the warm tubes boiled and displaced the contained air. The capacities of the various parts were so arranged that when *E* and *L* were full of liquid there was still some in the spiral and tube *M*, whilst when *E* and *L* were empty the level of the liquid in *I* was above the entrance of the spiral.

Having displaced the air as described above, the manometer and its connecting tube were exhausted through the tap *N* by means of an efficient water pump, *B* being kept closed. *B* was then turned to admit vapour into the manometer. By alternately filling and exhausting the manometer several times, the air was all displaced. Suction was now applied at *C* until the liquid level was nearly at the bottom of the bulb *E*, and at this stage, after the temperature had been constant for several minutes, a vapour pressure reading was taken. The whole process described above was now repeated until the vapour pressure was constant, when the temperature was varied, and a series of vapour-pressure readings was taken. The volumes of the manometer and its connecting tube were small, and did not require much vapour to fill them, consequently the composition of the liquid would not be much changed by the exhausting process; in any case, as the readings and subsequent samples were all taken after the exhaustion, any slight change would be of no importance.

It was found that after taking a series of vapour-pressure readings the pressure appeared to increase slightly. This was attributed to decomposition of the halide vapour by the tap grease with consequent production of hydrogen. To reduce any error caused by this, the manometer was occasionally exhausted during a series of readings. The vapour pressures were plotted against the temperatures, and from the curves the vapour pressure at any desired temperature could be calculated. These curves are referred to later in the paper.

Having obtained the vapour-pressure curve, it was necessary to obtain samples of the liquid and gas phases for analysis. For this purpose, it was necessary to isolate and absorb completely a portion of the liquid in order to get its true composition. This was accomplished by means of the bulb *L*. By means of the hydrogen pressure, the bulb *E* was filled with liquid, and by then applying pressure alternately at *C* and *K* and suitably opening the taps, *L* was alternately filled with and emptied of liquid to ensure having a true sample. Finally, a small quantity of liquid was left in *L*, and the hydrogen pressure applied at *J*, keeping the tap shut. Geissler tubes, as used for carbon dioxide absorption in combustions, were attached at *K* and *C* by rubber tubing, the taps being closed. On opening the tap *J*, the hydrogen pressure forced a few bubbles of gas into *L* and *E*, and left the connecting tube full of gas, thus separating the two portions of liquid. The taps *K* and *C* were now carefully opened. A stream of gas passed down the tube *J*, and at *O* divided into two portions. One stream bubbled through *L*, evaporating the contained liquid, which was absorbed by the alkali in the Geissler bulb attached to *K*. *P* is a fairly fine capillary tube, which served to prevent diffusion backwards of vapour from *L*. The other gas stream passed into *E* and down the tube to *H*, where it broke into bubbles at the constriction. The tube leading from *E* to *L* has a capillary constriction, which served to increase the velocity of the gas stream, and thus helped to prevent diffusion of vapour from *E* to *L*, which would cause an error in the analysis.

The bubbles of hydrogen, on forming at *H*, ran around the spiral *G*, which contained over a metre of glass tubing. These bubbles, as explained previously, caused thorough mixing of the liquid, and ensured it being of uniform composition, and at the same time became saturated with the gas phase in equilibrium with the liquid. Finally, the hydrogen saturated with the vapour passed through the tap *C* and through the attached Geissler bulb, where absorbable gases were collected. A little experience showed how much liquid it was necessary to have in L in order to obtain convenient analytical results, and also how long to pass the hydrogen through the spiral to get the gas composition.

When the absorption was complete, each Geissler bulb was removed, and its contents thoroughly mixed by blowing them from one bulb to the other. The solution was then blown into a beaker, and as only ratios were required it was not necessary to remove the whole contents, but it was necessary to have them thoroughly mixed before removal. Aliquot parts of the solution were removed for analysis by means of pipettes, the necessary volumes for convenient titration values being judged from knowledge of the approximate composition of the mixtures and from previous analyses.

Sulphur dioxide and hydrogen sulphide were determined by titration with $N/10$-iodine solution, and the halogen hydrides by Volhard's method, using $N/10$-silver nitrate and potassium thiocyanate. As silver sulphide is not easily dissolved by nitric acid, it was necessary to remove hydrogen sulphide from solutions before estimating the halogen. This was done by oxidation with sodium peroxide and subsequent removal of excess of hydrogen peroxide by boiling. The quantities of gas removed for an analysis were insufficient to change appreciably the composition of the liquid remaining. A series of analyses of gas and liquid was made at different temperatures, thus obtaining a number of values for the composition of the liquid which should agree, and other values for the composition of the gas which should either agree or show regular variation with temperature.

To prepare a fresh mixture, the cap Q was removed, a fine glass tube passed into I, and a portion of the liquid sucked out by means of a water pump. The cap was then replaced, and fresh liquid distilled in.

The apparatus was contained in a vacuum vessel measuring about 4·5 cm. by 20 cm., internal dimensions.

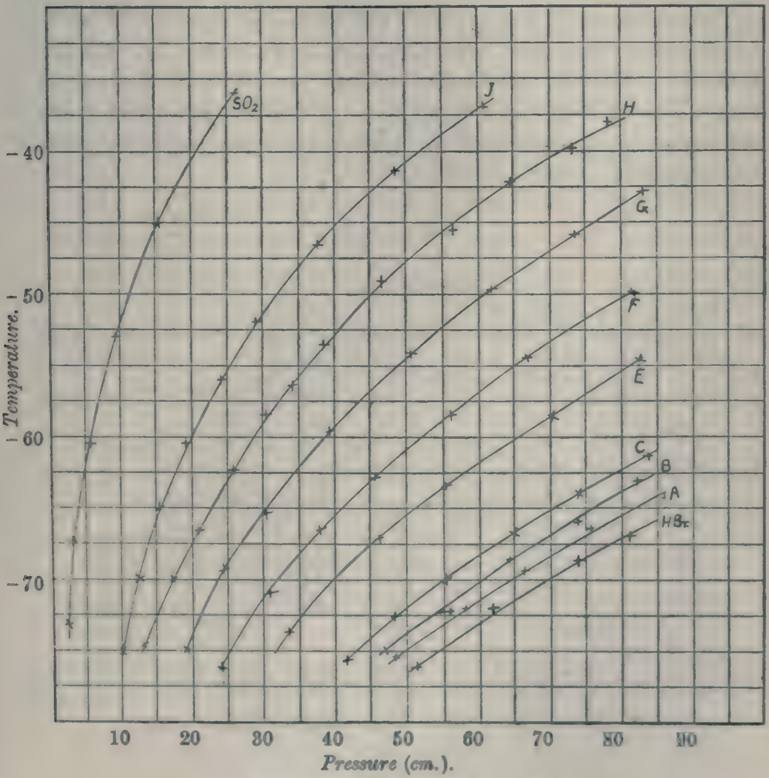
The apparatus we have described could be made on a larger scale if the liquids to be used were more easily prepared and less expensive. It might be useful at the ordinary temperature for liquids which are hygroscopic or decomposed by air. If used on the larger scale, it could be applied to liquids which cannot be directly absorbed or estimated, sufficient liquid being used to allow a quantity sufficient for analysis by physical measurements to be distilled out and condensed without appreciably changing the composition of the residue. With modern means of obtaining low temperatures, even very volatile substances might be thus condensed.

Experimental Results.

The experimental results are given in the following tables.

For several reasons it was possible to obtain data for the construction of complete vapour pressure-composition curves over a limited range of temperature only. The analyses could not be performed when the vapour pressure of the solution was greater than atmospheric, whilst, owing to the differences in the boiling points of the two constituent mixtures rich in the less volatile constituent, they could be analysed at a higher temperature than those containing more of the more volatile constituent. A lower limit was fixed by the lowest temperature that could be conveniently obtained with the liquid ammonia, whilst with the hydrogen iodide a limit was fixed by the freezing of solutions rich in that compound.

FIG. 2.



Sulphur dioxide—hydrogen bromide.

A vapour pressure-composition curve has been constructed for each pair of liquids at that temperature at which most complete data are available.

Portions of curves for other temperatures can be constructed from the data given.

Sulphur Dioxide and Hydrogen Bromide.

Table I gives the vapour-pressure readings for mixtures of sulphur dioxide and hydrogen bromide, whilst in table II is given, as a typical example, the results of the analyses of mixture *F*. The vapour pressure-temperature curves are shown in Fig. 2. The letters at the heads of the columns of tables I and II and the curves in Fig. 2 all refer to the same mixtures. Pressures are given in cm. of mercury. All compositions of mixtures are expressed as molecular percentages of halogen hydride.

TABLE I.

Mixture.										
HBr	Temp.	−76°	−72°	−68·6°	−66·8°					
	V. P.	51·7	61·7	73·9	80·9					
A.	Temp.	−75·5°	−72°	−69·3°	−66·4°	−64·3				
	V. P.	48·5	57·9	66·4	75·7	85·8				
B.	Temp.	−75°	−72·3°	−68·6°	−65·9°	−63°				
	V. P.	46·9	55·8	64·4	73·8	82·1				
C.	Temp.	−75·7°	−72·6°	−70°	−66·7°	−63·9°	−61·3°			
	V. P.	41·6	48·2	55·2	65·0	74·1	83·5			
E.	Temp.	−73·7°	−67·1°	−63·5°	−58·5°	−54·6°				
	V. P.	33·0	46·2	55·1	70·1	82·5				
F.	Temp.	−76·0°	−71°	−66·5°	−62·7°	−58·5°	−54·4°	−49·8°		
	V. P.	24·1	30·7	37·9	45·8	56·0	66·7	81·5		
G.	Temp.	−75·0°	−69·3°	−65·3°	−59·6°	−54·2°	−49·6°	−46·0°	−42·8°	
	V. P.	19·0	24·6	30·4	39·3	50·6	61·8	72·8	82·9	
H.	Temp.	−75·1°	−70·0°	−66·5°	−62·4°	−58·5°	−56·3°	−53·5°	−49·4°	
	V. P.	14·0	17·2	21·0	25·8	30·5	34·1	38·6	46·6	
	Temp.	−45·6°	−42·1°	−39·3°	−38·0°					
	V. P.	56·4	64·5	73·1	78·1					
J.	Temp.	−75·0°	−70·0°	−63·0°	−60·3°	−55·9°	−52·0°	−46·6°	−41·4°	−37·0°
	V. P.	10·0	12·3	15·3	19·2	24·1	29·0	37·7	48·6	60·7
SO_2	Temp.	−73·0°	−67·3°	−60·3°	−53·0°	−45·0°	−36·0°			
	V. P.	2·1	3·0	5·8	9·4	15·2	26·0			

TABLE II.

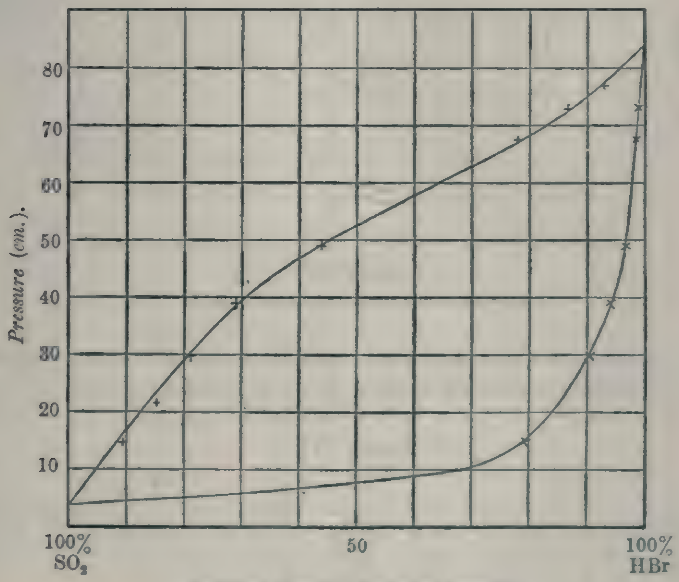
Mixture.	Temperature.	Molecular percentage of HBr (liquid).		Molecular percentage of HBr (gas).	
			Value used.		Value at −66°.
F.	−75°	28·5	29	95·3	
	−67·5	30		94·3	94
	−60·3	29		93·1	
	−53	28·5		92·2	

The samples of gas and liquid were usually taken first at the lowest temperature, then at the highest, followed by others at intermediate temperatures. An examination of table II shows that the temperature has a distinct effect on the composition of the gas, increasing temperature causing an increase in the relative quantity of sulphur dioxide in the gas phase.

The vapour pressure-concentration curve has been drawn for a temperature of −66°, and is shown in Fig. 3. If necessary, the gas composition at this temperature was calculated from the values at surrounding temperatures.

At lower temperatures the points do not fit so well to the curves, which, however, appear to conform to the same type. The type of curve is well known, and is of the general shape one might expect from a knowledge of the properties of the constituents and of the mixtures. The partial pressure curves have not been drawn. That for hydrogen bromide will nearly correspond with the total pressure curve, whilst the sulphur dioxide curve will lie almost along the line of zero pressure.

FIG. 3.



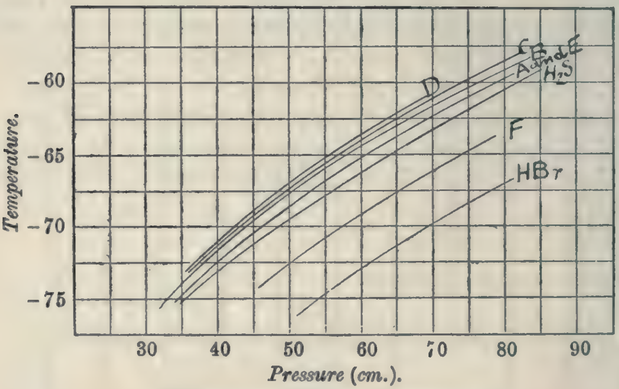
Sulphur dioxide—hydrogen bromide.

Hydrogen Sulphide and Hydrogen Bromide.

Table III contains the vapour-pressure readings for mixtures of hydrogen sulphide and hydrogen bromide. As before, pressures are given in cm. of mercury, and compositions of mixtures are expressed as molecular percentages of halogen hydride.

The vapour pressure-temperature curves are shown in Fig. 4. As the curves lie so closely together, the points through which they were drawn are not marked. Reference to the tables will show that the points fit the curves closely. By chance, mixtures *A* and *E* have the same vapour pressure, and are represented by the same curve *AE*. The curves show that a mixture of minimum vapour pressure and consequent maximum boiling point is formed.

FIG. 4.



Hydrogen sulphide—hydrogen bromide.

TABLE III.

Mix-ture.										
H_2S	Temp.	−75·1°	−73·1°	−71·0°	−69·0°	−66·6°	−65·0°	−63·0°	−61·0°	−59·3
	V. P.	35·3	39·8	45·6	52·6	58·6	64·5	70·9	77·6	85·3
A.	Temp.	−75·0°	−72·7°	−70·0°	−67·5°	−65·0°	−62·2°	−59·5°		
	V. P.	34·9	39·5	46·8	53·2	60·6	70·6	81·5		
B.	Temp.	−75·4°	−71·7°	−67·6°	−64·4°	−60·9°	−58·5°			
	V. P.	32·6	39·6	50·1	59·9	72·7	83·0			
C.	Temp.	−75·0°	−72·0°	−68·2°	−64·6°	−60·1°	−58·0°			
	V. P.	33·8	38·7	47·7	58·4	73·6	82·2			
D.	Temp.	−72·7°	−64·0°							
	V. P.	36·0	58·4							
E.	Temp.	−74·2°	−69·0°	−65·7°	−60·9°					
	V. P.	36·3	49·0	58·9	76·2					
F.	Temp.	−74·1°	−72·0°	69·0°	−63·8°					
	V. P.	46·4	51·2	60·7	78·3					

The gas composition was not so regular as with the sulphur dioxide mixtures, and, as a rule, the mean value has been taken in constructing the vapour pressure-concentration curve, which has been drawn for −70° (Fig. 5). The minimum referred to is well shown.

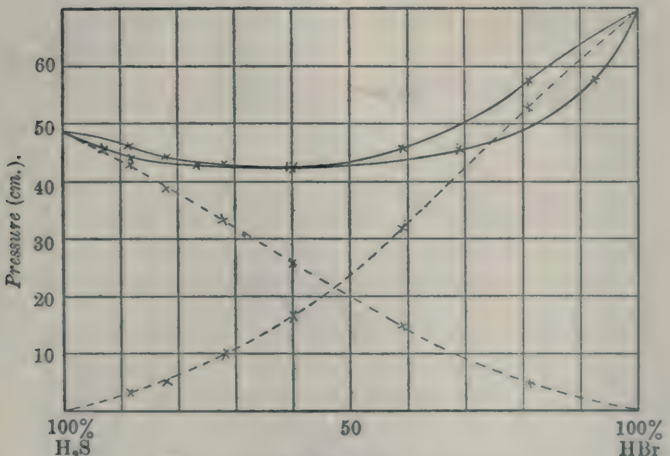
Ostwald has pointed out that in all cases the partial pressure curves of the components of a binary mixture must be symmetrical, being, in fact, mirror images of each other except as regards vertical measure. The partial pressure curves of hydrogen bromide and hydrogen sulphide, which are shown by dotted lines in Fig. 5, furnish an example of this.

Hydrogen Sulphide and Hydrogen Iodide.

Table IV gives the vapour-pressure readings for the mixtures of hydrogen sulphide and hydrogen iodide. The vapour pressure-composition curves are shown in Fig. 6.

Reference to Fig. 6 will show that the vapour-pressure measurements for pure hydrogen iodide have not been carried below the freezing point, which is about −52·5° by the thermometer used.

FIG. 5.



Hydrogen sulphide—hydrogen bromide.

Owing to the higher vapour pressure of the hydrogen sulphide, it was necessary to work at temperatures not much above −60° with mixtures rich in that constituent. To plot the complete vapour pressure-composition curve at −60°, we required the vapour pressure, not of solid hydrogen iodide, but of the supercooled liquid. This was obtained by exterpolation, the exterpolated portion of the curve being shown by the broken line.

Two separate series of experiments were performed with these substances, and are given in the tables as series I and series II.

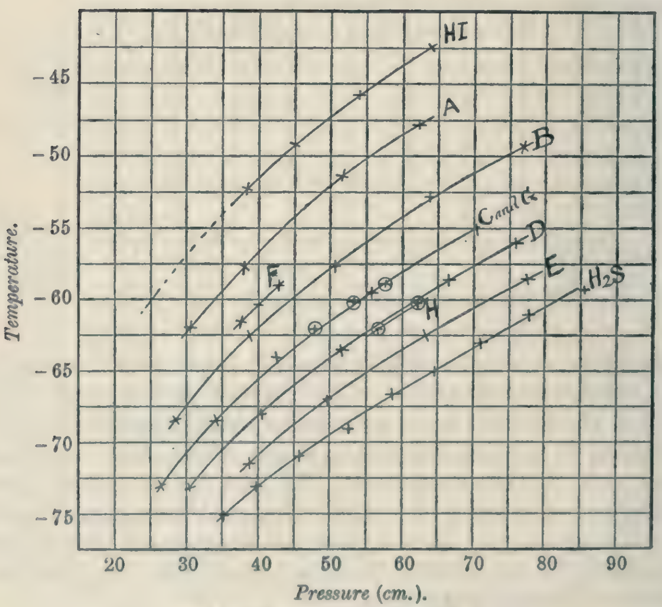
TABLE IV.—*Series I.*

Mixture.							
HI.	Temp.	−39·5°	−43·0°	−45·8°	−49·2°	−52·3°	
	V. P.	74·3	63·8	53·9	45·0	38·3	
A.	Temp.	−62·0°	−57·7°	−51·3°	−47·8°		
	V. P.	30·5	37·9	51·6	62·4		
B.	Temp.	−68·4°	−62·5°	−57·6°	−52·8°	−49·4°	
	V. P.	28·5	38·6	50·7	63·7	76·5	
C.	Temp.	−73·0°	−68·4°	−64·0°	−59·5°	−55·0°	52·5°
	V. P.	26·4	34·3	42·3	55·6	70·2	88·5
D.	Temp.	−73·0°	−68·0°	−63·5°	−58·5°	−56·0°	
	V. P.	30·2	40·4	51·5	66·6	75·7	
E.	Temp.	−71·5°	−67·0°	−62·5°	−58·5°		
	V. P.	38·8	49·6	63·1	77·3		

TABLE V.—*Series II.*

Mixture.				
F.	Temp.	−61·5°	−60·3°	−59·0°
	V. P.	37·6	40·0	42·9
G.	Temp.	−62·0°	−60·2°	−58·8°
	V. P.	48·0	53·4	57·6
H.	Temp.	−62·0°	−60·2°	—
	V. P.	56·6	62·0	—

FIG. 6.

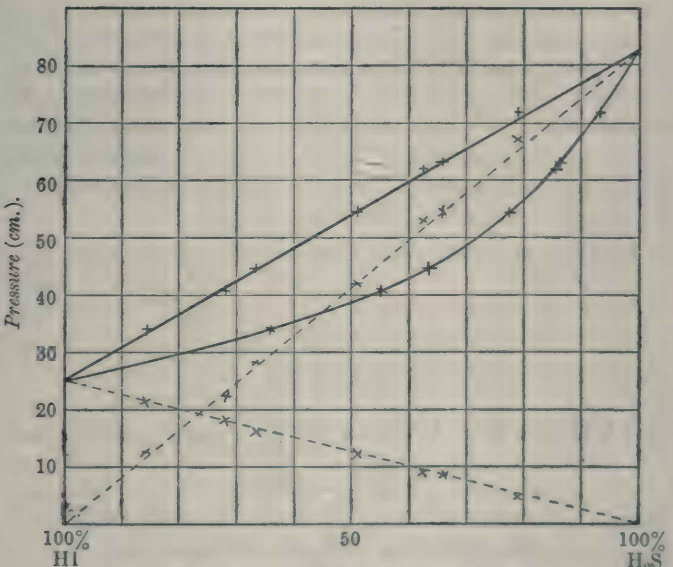


Hydrogen sulphide—hydrogen iodide.

The vapour pressure-composition curve at −60° is shown in Fig. 7. The partial pressure curves are shown by the dotted lines.

A comparison of Figs. 5 and 7 shows a surprising contrast in the nature of the curves obtained when hydrogen bromide and hydrogen iodide respectively are mixed with hydrogen sulphide. In the case of the former substance (Fig. 5), a well-marked minimum of vapour pressure is found. The occurrence of a minimum such as this is characteristic of a few pairs of substances, the majority of which, such as the mixtures of water with the mineral acids, present as their most striking characteristic the formation of highly ionised mixtures. Other systems presenting the same type of vapour pressure-concentration curves are mixtures of a few nitrogen bases with fatty acids, and in the case of these there is no doubt that combination occurs to a large extent.

FIG. 7.



Hydrogen sulphide—hydrogen iodide.

Roozeboom has pointed out that in nearly all cases where such minima occur we have independent evidence of (*a*) ionisation of one component, (*b*) combination between the components, or (*c*) association of one or both components.

From this point of view the behaviour of this pair of substances is the more remarkable, since there is no evidence of appreciable ionisation in any of the mixtures, and measurements of the molecular surface energy which were made by Steele, McIntosh, and Archibald yielded no evidence of association either of hydrogen sulphide or of hydrogen bromide, and did not point to any difference in the molecular complexity of hydrogen bromide and hydrogen iodide. Of the three alternatives suggested by Roozeboom, there remains therefore only the possibility of compound formation between hydrogen bromide and hydrogen sulphide, and of this no evidence is yet forthcoming.

The system hydrogen sulphide and hydrogen iodide is interesting as adding another to the very short list of pairs of liquids which form ideal solutions, solutions for which Raoult's law applies over the whole range of concentration. This is shown in Fig. 7 by the occurrence of straight lines for the vapour pressure-liquid concentration curve, and for the two partial pressure curves.

In conclusion, we desire to state that the greater part of the expense of the investigation has been defrayed by a grant from the Royal Society. We also wish to express our indebtedness to Messrs. Felton, Grimwade & Co., of Melbourne, for their kindness in presenting us with considerable quantities of liquefied ammonia, and to Mr. H. J. Grayson, of this University, who specially ruled the micrometer scale which we have employed.

THE UNIVERSITY,
MELBOURNE.

CCLXVIII.—*The Volume of a Solute in Solution.*

By DAN TYRER.

THE changes of volume which occur when substances dissolve are of interest as affording valuable criteria of the nature of solutions. This study has, however, in the past been nearly always concerned with aqueous, and less frequently with alcoholic, solutions, which we now know to be abnormal in the sense that in such cases we are not dealing with simple molecular mixtures of solute and solvent. It is only in the case of very dilute aqueous solutions of salts, where the solute is practically totally dissociated, and in the case of aqueous solutions of non-electrolytes, that any regularities have been discovered.

Valson (*Compt. rend.*, 1871, **73**, 441) found that the difference between the volumes of two salts M_1R and M_3R in dilute solutions is constant—independent of the nature of the acid radicle R; Nicol (*Chem. News*, 1882, **45**, 37) discovered practically the same thing. Taking into consideration the degree of ionisation, Traube (*Ber.*, 1894,

27, 3173) has been able to determine what he terms the "atomic solution volumes" of most of the elements, and has shown that most of the monatomic metals have the same volume in dilute solution. In several cases of non-electrolytes in water, it has been found that the volume of the solute in solution is constant—independent of the concentration. For example, Wanklyn (*Chem. News*, 1892, **65**, 122) found this to be the case for aqueous sugar solutions (see also Traube, *Annalen*, 1896, **290**, 43).

In general, however, it is found that with aqueous and alcoholic solutions the specific volume of the solute in solution diminishes with increase of dilution (Gerlach, *Zeitsch. anal. Chem*, 1888, **28**, 466; Schröder, *J. Russ. Phys. Chem. Soc.*, 1886, **18**, 25; Tammann and Hirschberg, *Zeitsch. physikal. Chem.*, 1894, **13**, 543; Traube, *Annalen*, 1896, **290**, 43). This diminution is probably due partly to ionisation and partly to changes in molecular complexes, such as the formation of solvates and variations in the molecular complexity of the solvent. In most cases of aqueous solution, the volume change brought about by the dissolution of the solute is a positive quantity, but in a few cases it has a negative value, for example, copper sulphate and sodium nitrate.

On the other hand, with non-associated solvents and solutes very little work has been done.

Beilby (Trans., 1883, **43**, 138) found that the specific volume of paraffin wax dissolved in the paraffin hydrocarbons was approximately equal to the specific volume which the melted paraffin wax would have at the same temperature. Lumsden (Trans., 1907, **91**, 24) examined the change in molecular volume of several solutes dissolved in several organic solvents with change of temperature, and found that the volume increased quite regularly to temperatures above the melting points or boiling points of the pure solvent.

Forch (*Ann. Physik*, 1905, [iv], **17**, 1012) determined the molecular volume of naphthalene in several solvents, such as benzene, chloroform, etc., and found that the molecular volume was constant—independent of the concentration and of the solvent (except in the case of ether), and equal approximately to the calculated molecular volume which liquid naphthalene would have at the same temperature.

Dawson (this vol., pp. 1041, 1896) found almost exactly the same thing for solutions of naphthalene and iodine in various organic solvents. The influence of the solvent was found to be rather considerable, however, in the second case, and this was considered as probably due to the formation of molecular complexes.

The object of the present work is to extend the above observations to other cases, to ascertain whether the volume in solution of a given mass of a solute is independent of the concentration, and to what extent it is independent of the solvent.

Method and Apparatus.

Two methods have been used for measuring the specific volumes of the solutions, the dilatometrical and the pyknometrical.

The dilatometer consisted of a glass bulb of about 40 c.c. capacity blown on the end of a long tube carefully graduated in mm. It was calibrated by weighing it filled with boiled distilled water (cooled in a vacuum) to various points on the stem. By this means the dilatometer was calibrated for every cm. reading along the stem. To determine the correction for the thermal expansion of the dilatometer itself, the calibrations were repeated at various other temperatures. Finally, these results were confirmed by substituting pure distilled mercury for the water and repeating the observations. All the weighings were reduced to a vacuum, and corrections were made for the curved surface of liquid in the stem of the dilatometer. The instrument was recalibrated repeatedly throughout the course of the experiments, and the slight changes which were found to have occurred were taken into account. With fairly volatile liquids, such as benzene, an appreciable quantity of the substance exists in the state of vapour in the stem. To diminish this and at the same time to prevent loss by evaporation during the course of an experiment, the open end of the stem was closed by a thin glass rod which was made to slide up and down within the stem, and could be gradually raised as the liquid expanded and rose up the stem.

The dilatometer was heated in a large bath of water, insulated from draughts. The temperature could be easily controlled to 0·01° for a time sufficient to allow the temperature of the liquid in the dilatometer to reach equilibrium. The bath was stirred with a vertically acting stirrer worked with a small motor. Two thermometers were used, both graduated in 1/10ths of a degree and readable to 1/100ths, one over a range of 0° to 50°, the other from 50° to 100°. The thermometers were calibrated to 0·01° by comparison with a standard, and the calibrations were repeated at frequent intervals throughout the course of the experiments and corrections made for any slight variations observed. All the readings of the dilatometer and thermometers were made with the help of a small telescope.

Each solution used was prepared by direct weighing of the solute and solvent, great care being taken to prevent loss by evaporation.

Details in regard to purity of the materials are given as they arise.

The observed results were made at irregular intervals of temperature (usually every 5 or 6 degrees) between 15° and a short distance below the boiling point of the pure solvent. In order to obtain comparable results, the experimental values were plotted on a large sheet of cross section paper, of a sufficient scale to permit of readings of specific volumes to 0·00005. The mean probable error in the specific volume determinations by the dilatometer is, however, more than this, being about 0·0001. This degree of accuracy is not sufficient for very dilute solutions, and therefore experiments with the dilatometer have been confined to solutions of a moderate concentration.

If A is the percentage concentration of a solution (grams of solute per 100 of solvent), S_1 the specific volume of that solution, and S_0 the specific volume of the pure solvent at the same temperature, then the change in volume due to dissolution of A grams of the solute is $(100+A)S_1 - 100S_0$, and the specific volume of solute in the solution is

$$v = \frac{(100+A)S_1 - 100S_0}{A}.$$

The values of v at various temperatures have been found by the dilatometer for two cases—phenanthrene and *m*-dinitrobenzene in various solvents.

The following solvents have been used: (*a*) Benzene, (*b*) toluene, (*c*) acetic ester, (*d*) chloroform, (*e*) carbon tetrachloride.

The "pure" substances, obtained from Kahlbaum, were redistilled or recrystallised several times before using.

The Specific Volume (v) *of Phenanthrene in Various Solvents.*

The phenanthrene used was Kahlbaum's. To test its purity a small sample was recrystallised, and the melting point carefully determined. It was found to melt at the same temperature as the original specimen.

In the following table are given the values of the specific volumes of solutions of phenanthrene at various concentrations in the several solvents, with the calculated specific volumes (v) in solution:

A = percentage concentration of solution (grams solute per 100 grams solvent).
S_0 = specific volume of pure solvent.
S_1 = specific volume of solution.
v = specific volume of the solute in solution.
T = temperature.

In Benzene.

		A = 4·199.		*A* = 7·797.		*A* = 15·894.	
T.	S_0.	S_1.	*v.*	S_1.	*v.*	S_1.	*v.*
15°	1·1307	1·1214	0·899	1·1135	0·892	—	—
20	1·1379	1·1282	0·895	1·1202	0·893	1·1039	0·889
30	1·1521	1·1419	0·895	1·1336	0·896	1·1164	0·891
40	1·1664	1·1556	0·899	1·1471	0·899	1·1292	0·895
50	1·1810	1·1699	0·907	1·1610	0·904	1·1420	0·896
60	1·1962	1·1847	0·911	1·1751	0·905	1·1554	0·898
70	1·2122	1·1997	0·901	—	—	1·1697	0·902

In Toluene.

		A = 3·197.		*A* = 5·493.		*A* = 11·712.		*A* = 27·297.	
T.	S_0.	S_1.	*v.*	S_1.	*v.*	S_1.	*v.*	S_1.	*v.*
15°	1·1488	1·1407	0·886	1·1348	0·881	1·1207	0·881	1·0918	0·883
20	1·1551	1·1467	0·886	1·1408	0·882	1·1264	0·881	1·0970	0·884
30	1·1678	1·1590	0·885	1·1530	0·883	1·1381	0·884	1·1078	0·887
40	1·1806	1·1716	0·890	1·1652	0·885	1·1500	0·889	1·1189	0·894
50	1·1936	1·1843	0·891	1·1778	0·889	1·1622	0·893	1·1300	0·897
60	1·2071	1·1975	0·897	1·1907	0·893	1·1746	0·897	1·1414	0·901
70	1·2212	1·2113	0·901	1·2043	0·897	1·1874	0·899	1·1530	0·903

In Acetic Ester.

		A = 6·922.		*A* = 9·149.		*A* = 18·832.	
T.	S_0.	S_1.	*v.*	S_1.	*v.*	S_1.	*v.*
15°	1·1022	1·0923	0·949	1·0828	0·869	—	—
20	1·1101	1·0988	0·937	1·0907	0·867	1·0726	0·873
30	1·1259	1·1143	0·946	1·1040	0·865	1·0852	0·868
40	1·1416	1·1296	0·956	1·1185	0·866	1·0987	0·871
50	1·1580	1·1452	0·961	1·1335	0·866	1·1126	0·872
60	1·1750	1·1616	0·967	1·1493	0·868	1·1273	0·874
70	1·1933	—	—	—	—	1·1426	0·874

In Carbon Tetrachloride.

		A = 2·873.		*A* = 4·575.	
T.	S_0.	S_1.	*v.*	S_1.	*v.*
15°	0·6241	0·6306	0·858	0·6347	0·866
20	0·6276	0·6344	0·874	0·6384	0·875
30	0·6349	0·6421	0·891	0·6460	0·891
40	0·6430	0·6499	0·892	0·6538	0·891
50	0·6512	0·6579	0·891	0·6616	0·890
60	0·6596	0·6661	0·893	0·6697	0·890
70	0·6685	0·6746	0·889	0·6781	0·888

It will be seen from the above tables that the values of *v*, as a rule, increase slightly, but regularly, with increase in temperature. The values in acetic ester, however, show some small variations from this rule, and these are repeated (as will be pointed out later) in other cases. The effect of concentration on the value of *v* seems very slight, except, again, in the case of acetic ester. Small divergences appear with the more dilute solutions, but here it is to be considered that the experimental error in the value of (v) is much greater than in the more concentrated solutions. For example, an error of 0·0001 in the specific volume of the solution for a concentration of 4 per cent. makes an error of about 0·004 in the value of v. Again, most of the values of the specific volume of the solutions for temperatures of 15° and 70° have been obtained by extrapolation, and therefore, in some cases, the experimental error may be greater than the average.

The influence of the solvent seems slight, but appreciable. The values of v in benzene, for example, are distinctly higher than those in toluene and carbon tetrachloride.

The Specific Volume of m-*Dinitrobenzene in Various Solvents.*

In Benzene.

	$A=4·823$		$A=8·939$		$A=16·230$	
T.	S_1.	v.	S_1.	v.	S_1.	v.
15°	1·1101	0·682	—	—	1·0684	0·684
20	1·1169	0·683	1·1002	0·678	1·0746	0·685
30	1·1304	0·680	1·1132	0·678	1·0871	0·686
40	1·1441	0·682	1·1267	0·681	1·0997	0·689
50	1·1581	0·683	1·1403	0·684	1·1126	0·690
60	1·1724	0·681	1·1544	0·686	1·1258	0·692
70	—	—	1·1689	0·684	1·1395	0·692

In Toluene.

	$A=4·092$		$A=7·675$		$A=15·595$	
T.	S_1.	v.	S_1.	v.	S_1.	v.
15°	—	—	1·1143	0·665	1·0840	0·668
20	1·1354	0·654	1·1203	0·667	1·0895	0·669
30	1·1477	0·656	1·1323	0·670	1·1009	0·672
40	1·1601	0·659	1·1444	0·672	1·1124	0·675
50	1·1726	0·658	1·1567	0·675	1·1241	0·678
60	1·1856	0·659	1·1694	0·679	1·1361	0·681
70	1·1982	—	1·1824	0·677	1·1484	0·680

In Acetic Ester.

	$A=3·722$		$A=6·416$		$A=16·508$	
T.	S_1.	v.	S_1.	v.	S_1.	v.
15°	—	—	1·0768	0·679	—	—
20	1·0945	0·676	1·0837	0·672	1·0478	0·670
30	1·1093	0·665	1·0983	0·668	1·0612	0·669
40	1·1246	0·668	1·1132	0·670	1·0749	0·671
50	1·1404	0·668	1·1287	0·672	1·0890	0·671
60	1·1569	0·671	1·1448	0·673	1·1036	0·671

In Chloroform.

		$A=2\cdot964$		$A=7\cdot017$	
$T.$	$S_0.$	$S_1.$	$v.$	$S_1.$	$v.$
15°	0·6683	0·6677	0·649	0·6678	0·668
20	0·6726	0·6721	0·657	0·6718	0·661
30	0·6812	0·6806	0·661	0·6801	0·664
40	0·6902	0·6895	0·664	0·6886	0·665
50	0·6995	0·6984	0·659	0·6974	0·667
60	0·7092	0·7075	0·648	0·7061	0·662

m-Dinitrobenzene is probably not so "normal" a substance as phenanthrene, for the nitro-compounds show, as a rule, an appreciable amount of molecular association. It will be noticed from the above tables that in all the solvents there is a slight increase in the specific volume of the solute in solution with increase of concentration, and the values of v vary more than in the case of phenanthrene from one solvent to another.

Determinations with the Pyknometer.

Two pyknometers have been used, one of small volume (about 5·2 c.c.) for large concentrations, and the other (about 14·5 c.c.) for the more dilute solutions. Both pyknometers were made of fused quartz, pyknometers of this material possessing the great advantage over glass instruments of changing only very slightly in volume when heated, and of being much less soluble in water. They were provided with small ground glass caps for the ends of the capillary tubes. Their volumes were determined to 0·0001 c.c. by weighing them filled with air-free distilled water at 25°, taking the specific volume of water at this temperature to be 1·002937. All the determinations were made at the constant temperature of 25·00°, the pyknometers being immersed in a large volume of water maintained at this temperature by a sensitive thermoregulator. The weighings of the pyknometer filled with the solutions were made to 0·0001 gram. Every solution investigated was made up by direct weighing of solute and solvent, and to diminish the error introduced by the unavoidable loss by evaporation of a slight amount of the solvent, several times more solution was prepared than was necessary to fill the pyknometer. All the weighings were reduced to a vacuum. The mean probable error in the specific volume determinations by the smaller pyknometer is about 0·00006, and with the larger pyknometer about 0·00002. When the concentration of the solution was more than about 8 per cent., the specific volume was determined with the small pyknometer; for smaller concentrations the larger pyknometer was used.

In the following tables are given the results of the determinations for the constant temperature of 25·00° of several solutes in various solvents and at various concentrations.

The Specific Volume of p-*Dibromobenzene in Various Solvents at* 25·00°.

In the following tables:

A = percentage concentration of the solution.
S_1 = specific volume of solution at 25·00°.
v = specific volume of solute in solution at 25·00°.
S_0 = specific volume of solvent at 25·00°.

In Benzene ($S_0 = 1·14497$).

A.	S_1.	v.
5·067	1·11453	0·513
9·863	1·08853	0·516
22·935	1·02689	0·512
37·895	0·97129	0·514

In Toluene ($S_0 = 1·16094$).

A.	S_1.	v.
3·919	1·13635	0·508
8·395	1·11054	0·508
15·782	1·07155	0·505
30·966	1·00682	0·509

In Acetic Ester ($S_0 = 1·11794$).

A.	S_1.	v.
3·268	1·09769	0·479
5·599	1·08516	0·499
7·642	1·07443	0·505
14·097	1·04233	0·506
25·157	0·99555	0·508

In Chloroform ($S_0 = 0·67688$).

A.	S_1.	v.
2·222	0·67323	0·507
4·355	0·66965	0·505
9·973	0·66135	0·505

In Carbon Tetrachloride ($S_0 = 0·63121$).

A.	S_1.	v.
2·615	0·62809	0·508
7·710	0·62230	0·507

In Ethyl Bromide ($S_0 = 0·69521$).

A.	S_1.	v.
3·697	0·68808	0·494
4·008	0·68762	0·496

In Carbon Disulphide ($S_0 = 0·79638$).

A.	S_1.	v.
3·979	0·78555	0·513
8·704	0·77366	0·512
11·087	0·76835	0·515

In Ethyl Ether ($S_0 = 1·41236$).

A.	S_1.	v.
2·788	1·38640	0·456
8·099	1·34107	0·461
8·461	1·33855	0·466
18·638	1·26362	0·465

In Hexane ($S_0 = 1·48795$).

A.	S_1.	v.
4·371	1·44665	0·502

In iso*Amyl Acetate* ($S_0 = 1·15998$).

A.	S_1.	v.
8·648	1·10879	0·510

It will be seen from the above tables that the specific volume (v) of the dibromobenzene remains constant (within the errors of experiment) for any one solvent with the exception of acetic ester and ethyl ether, with which it increases with increase of the concentration. The nature of the solvent in the other cases has a distinct effect on the value of v, varying from 0·495 in ethyl bromide to 0·513 in benzene, or about 3·5 per cent.

The Specific Volume of Diphenyl in Various Solvents at 25·00°.

In Benzene.

A.	S_1.	v.
2·003	1·14155	0·970
5·492	1·13588	0·970
10·736	1·12767	0·967
14·876	1·12175	0·965
18·118	1·11738	0·965

In Toluene.

A.	S_1.	v.
2·699	1·15570	0·961
4·515	1·15238	0·963
9·814	1·14291	0·959
13·543	1·13751	0·964
31·867	1·11279	0·962

In Acetic Ester.

A.	S_1.	v.
2·000	1·11459	0·947
4·908	1·11009	0·950
9·147	1·10369	0·947
11·558	1·10095	0·953
20·764	1·08902	0·949

In Chloroform.

A.	S_1.	v.
1·654	0·68131	0·947
4·375	0·68859	0·955
5·616	0·69204	0·962
11·457	0·70635	0·964
15·136	0·71490	0·966

In Hexane.

A.	S_1.	v.
2·121	1·47639	0·931
6·877	1·45240	0·935

In iso*Amyl Acetate.*

A.	S_1.	v.
7·467	1·14579	0·956
12·911	1·13672	0·956

In Nitrobenzene ($S_0 = 0·8350$).

A.	S_1.	v.
1·934	0·83760	0·967
4·438	0·84103	0·975

In Carbon Disulphide.

A.	S_1.	v.
3·958	0·80315	0·974
13·253	0·81753	0·977

In Ethyl Ether.

A.	S_1.	v.
2·160	1·40152	0·900
3·788	1·39356	0·898
8·761	1·37057	0·894
12·617	1·35310	0·891

It will be noticed in the case of diphenyl that variations from constancy of the value of v are more marked than in the previous case. In benzene v decreases slightly with increase of concentration, whilst in chloroform the opposite is the case. As before, the values in ether are much lower than in any of the other solvents, and a slight fall of v occurs with increase of the concentration. The values in carbon disulphide and nitrobenzene are much greater than the average. The percentage difference between the highest (0·977) and the lowest (0·891) is about 9.

The Specific Volume of Acenaphthene on Various Solvents at 25·00°.

In Benzene.

A.	S_1.	*v.*
1·904	1·14054	0·907
4·705	1·13456	0·913
8·480	1·12674	0·912
14·370	1·11610	0·915

In Toluene.

A.	S_1.	*v.*
2·143	1·15572	0·911
5·644	1·14753	0·909
10·188	1·13784	0·911
21·108	1·11756	0·912

In Acetic Ester.

A.	S_1.	*v.*
3·769	1·10984	0·895
7·022	1·10324	0·894
12·246	1·09422	0·900

In Chloroform.

A.	S_1.	*v.*
1·515	0·68064	0·931
4·131	0·68645	0·919
7·963	0·69461	0·918
15·207	0·70920	0·922

In Hexane.

A.	S_1.	*v.*
3·205	1·46880	0·871
4·945	1·45910	0·875

In Nitrobenzene.

A.	S_1.	*v.*
2·915	0·83763	0·924
4·020	0·83858	0·925

In Ethyl Ether.

A.	S_1.	*v.*
3·962	1·39015	0·829
6·829	1·37509	0·829
8·083	1·36922	0·835

As in the previous cases, low values of *v* for acenaphthene are shown in ethyl ether and hexane, and high values in nitrobenzene. The value increases with the concentration in acetic ester. The value 0·931 in chloroform is very probably too high.

The Specific Volume of Benzil in Various Solvents.

In Benzene.

A.	S_1.	*v.*
1·931	1·13942	0·850
6·030	1·12808	0·848
6·324	1·12752	0·851
13·962	1·10903	0·851
20·558	1·09488	0·851

In Toluene.

A.	S_1.	*v.*
2·863	1·15225	0·848
4·358	1·14778	0·846
7·183	1·13968	0·844
20·401	1·10818	0·850
28·260	1·09264	0·851

In Acetic Ester.

A.	S_1.	*v.*
2·034	1·11221	0·830
4·411	1·10601	0·835
7·517	1·09810	0·834
17·839	1·07552	0·837

In Chloroform.

A.	S_1.	*v.*
2·074	0·68018	0·843
3·975	0·68315	0·842
10·508	0·69290	0·846
18·093	0·70349	0·851

The Specific Volume of Benzil in Various Solvents—(continued).

In Nitrobenzene.

A.	S_1.	*v.*
1·836	0·83570	0·868
4·869	0·83662	0·868

In Ethyl Ether.

A.	S_1.	*v.*
2·145	1·39909	0·781
5·062	1·38164	0·775
11·723	1·34574	0·777

The value of *v* in toluene shows irregularities at small concentrations, but assumes a value identical with that in benzene at higher concentrations. In acetic ester there is a consistent increase with increase of concentration. Again, in nitrobenzene the values are highest, and lowest in ether.

The Specific Volume of Azobenzene in Various Solvents at 25·00°.

In Benzene.

A.	S_1.	*v.*
1·984	1·14060	0·920
3·971	1·13625	0·916
7·866	1·12867	0·921
15·799	1·11421	0·919

In Toluene.

A.	S_1.	*v.*
2·924	1·15367	0·905
4·670	1·14985	0·912
9·346	1·13974	0·913
12·006	1·13471	0·916

In Acetic Acid.

A.	S_1.	*v.*
2·013	1·11364	0·900
4·873	1·10777	0·899
11·757	1·09527	0·902
14·204	1·09106	0·902

In Chloroform.

A.	S_1.	*v.*
3·216	0·68419	0·910
8·087	0·69452	0·912
12·143	0·70295	0·918

In Ethyl Ether.

A.	S_1.	*v.*
2·055	1·40123	0·860
6·192	1·37957	0·850
9·326	1·36359	0·841
19·892	1·31929	0·851

In Carbon Disulphide.

A.	S_1.	*v.*
1·035	0·79763	0·918
6·670	0·80475	0·930
16·442	0·81539	0·931

In Hexane.

A.	S_1.	*v.*
1·405	1·47974	0·895
8·811	1·46632	0·899

In Nitrobenzene.

A.	S_1.	*v.*
1·879	0·83689	0·929
4·689	0·83939	0·931

The Specific Volume of Durene in Various Solvents at 25·00°.

In Benzene.

A.	S_1.	v.
2·663	1·14555	1·167
7·571	1·14591	1·159
10·572	1·14636	1·159
15·787	1·14669	1·158
18·951	1·14624	1·154
30·322	1·14657	1·159

In Toluene.

A.	S_1.	v.
3·032	1·16083	1·157
7·262	1·16013	1·149
7·080	1·15992	1·145
19·621	1·15758	1·140

In Acetic Ester.

A.	S_1.	v.
1·144	1·11798	1·122
3·039	1·11882	1·147
9·160	1·12005	1·132
14·326	1·12105	1·143

In Chloroform.

A.	S_1.	v.
1·983	0·68636	1·168
4·876	0·69941	1·163
11·286	0·72558	1·157
16·167	0·74363	1·159

In Hexane.

A.	S_1.	v.
2·632	1·47838	1·114
10·903	1·45203	1·123
16·185	1·45099	1·222

In Nitrobenzene.

A.	S_1.	v.
2·058	0·84094	1·125
6·129	0·85196	1·127

It will be noticed that in most cases the value of *v* changes with the concentration. Notice the abnormally low values in nitrobenzene and comparatively high values in hexane as compared with the values in solvents in the other cases.

The Specific Volume of Triphenylmethane in Various Solvents at 25·00°.

In Benzene.

A.	S_1.	v.
1·577	1·14140	0·930
2·565	1·13929	0·927
7·290	1·13010	0·926

In Toluene.

A.	S_1.	v.
4·007	1·15131	0·916
7·976	1·14335	0·922
12·558	1·13458	0·917
21·781	1·11815	0·921

In Acetic Ester.

A.	S_1.	v.
1·810	1·11403	0·900
6·774	1·10521	0·917
10·490	1·09913	0·919

In Chloroform.

A.	S_1.	v.
2·748	0·68340	0·919
7·333	0·69373	0·923
7·551	0·69442	0·927
10·138	0·69997	0·928

In Hexane.

A.	S_1.	v.
1·892	1·47690	0·893
8·105	1·46998	0·891

In Ethyl Ether.

A.	S_1.	v
1·571	1·40391	0·865
8·507	1·36896	0·859

The above case is of particular interest, because triphenylmethane crystallises from benzene with one molecule of benzene of crystallisation (Kekulé and Franchimont, *Ber.*, 1872, **5**, 967). Moreover, it is probable, although not conclusive, that in solution in benzene a portion at least of the triphenylmethane exists in combination with the benzene. This does not, however, seem to affect at all considerably the value of (v). It is unfortunate that a limiting solubility prevents the extension of the experiments in this case any further.

It might be stated from a consideration of the above tables, that the specific volume of the solute in a normal solvent is approximately a constant independent of the concentration of the solution, and, with certain limitations, independent of the solvent. Although the term "specific volume of solute in solution" or "specific solution volume" has been used throughout this paper, it is not intended to imply that this represents the actual volume occupied by the solute in the solution, but the term is used from considerations of usage and simplicity. It has been usual with other investigators to express the results in terms of the molecular solution volume, but as no particular advantages appear to accrue from this method, the results here have been left in terms of the specific solution volume.

It has been shown repeatedly in a few cases that the volume of the solute in solution is equal to the volume occupied by the same weight of the solute when in the liquid state at the same temperature (Beilby, *loc. cit.*; Lumsden, *loc. cit.*; Forch, *loc. cit.*; Dawson, this vol., p. 1041). Now if the rule that the specific volume of the solute in solution is independent of the concentration holds to a concentration of 100 per cent. (that is, pure liquid solute)—and it has been shown in the above tables that it holds to comparatively large concentrations—the above observation follows at once.

In spite of a very close agreement between the values of v for a given solute in many of the solvents, there is, however, a distinct difference between the values of v in one solvent from the values in another. If the tables be inspected, it will be noticed that there seems to be some connexion between the nature of the solvent and the variation of the value of the specific solution volume of the solute from a certain mean value. For example, in every case the values in ether are lowest and those in carbon disulphide or nitrobenzene highest. If we arrange the solvents in order of magnitude of the specific solution volume of a solute, we obtain approximately the following sequence in every case except durene: (1) carbon disulphide, (2) nitrobenzene, (3) benzene, (4) toluene, (5) chloroform, (6) acetic ester, (7) hexane, (8) ethyl ether.

On the other hand, Dawson (*loc. cit.*) showed that in the two cases he investigated (iodine and naphthalene) no such similarity in arrangement was observable. The order for naphthalene is, however, very similar to the above. The two cases, iodine and durene, are quite apart, showing an entirely different order of arrangement of solvents. And it will be seen from the table that the specific volume of durene in solution varies also with the concentration, and this is strong evidence that in this case chemical changes occur in the solution, such as association or dissociation, for, in aqueous solutions where these chemical changes are known to take place, similar variations of the volume of the solute are observed.

This, however, will not suffice to explain the influence of the solvent. Let us consider the matter from the point of view of the molecular theory. In the ideal case no change in volume occurs on formation of a solution whatever the nature of the solvent. That is to say, the space taken up by each molecule of the solute is independent of the nature of the surrounding molecules. Now, in virtue of its kinetic energy, each molecule in a liquid exerts a certain pressure, which is proportional to the value of this energy, and depends also on the mean distance between two adjacent molecules. This pressure is counterbalanced by a molecular force of attraction. Therefore if a molecule of a solute, when surrounded by an atmosphere of solvent molecules, is to occupy the same volume as in its own liquid at the same temperature, then the attractive force acting on the molecule must be the same in both cases. If this attractive force is greater, there will ensue a closer grouping of solvent molecules around each molecule of solute (this does not mean that the two necessarily combine), and the observed specific solution volume of the solute will be diminished. This attractive force is identical with the force which undoubtedly plays a part in the dissolution of a solute, and, to some extent, the solubility (if small) might be regarded as a measure of this attractive force, but other factors come into consideration complicating the matter (see this vol., p. 1778).

In the contraction or expansion of the solvent its compressibility must be taken into consideration. The extent of this contraction or expansion will depend on two factors, namely: (1) the force of attraction between the molecule of solute and the surrounding solvent molecules; (2) the pressure or force necessary to bring about a very small change in the mean distance between the molecules of the solvent. The latter factor is the more important, and is approximately proportional to the product of the compressibility, β, and the molecular volume, V. If we arrange the solvents used in the above experiments in order of the values of βV, we get approximately the following sequence: (1) carbon disulphide, (2) benzene, (3) toluene, (4) chloroform, (5) ethyl acetate, (6) hexane, (7) ethyl ether.

This is exactly the same order of arrangement as given above for the variation of the specific volume of a solute. This is strong evidence in favour of the view that a connexion exists between the compressibility of a solvent and the volume which a solute, when dissolved in it, takes up. There is, however, the other factor to be considered. It is probable that with substances of nearly equal molecular solubility, this factor is constant, but at this stage of the subject there is not sufficient experimental data to make a systematic examination of the hypothesis.

In the ideal case when the attraction of the molecules of the solvent for a molecule of a dissolved solute is equal to the attraction exerted on the molecule when present in the pure liquid solute at the same temperature, the volume change occurring on the formation of the solution will be due entirely to the solute, and the property will be strictly additive.

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CCLXIX.—*Studies of Dynamic Isomerism. Part XII. The Equations for Two Consecutive Unimolecular Changes.*

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THE problem considered in the following pages is to determine the course of a chemical change which proceeds in two stages, each reversible and each obeying the unimolecular law. Two cases are considered:

(1) That in which the total quantity of material is constant, as is usually the case when isomeric changes are studied in solution.

(2) That in which the concentration of one of the constituents is kept constant, as, for instance, when isomeric change takes place in a solution saturated with one of the isomerides.

Work in this direction has already been done by Harcourt and Esson (*Phil. Trans.*, 1866, **156**, 193) and by Mellor (*Chemical Statics and Dynamics*, Chapter V), who has given the equations for two consecutive non-reversible actions: $X \rightarrow Y \rightarrow Z$ (*loc. cit.*, pp. 98, 114), and has calculated the course of the action in one particular case. P. V. Bevan (*Phil. Trans.*, 1904, *A*. **202**, 71) has given the equations, and has calculated one series of values for the case $X \rightleftarrows Y \rightarrow Z$.

Finally, Rakowski (*Zeitsch. physikal. Chem.*, 1906, **57**, 321) has investigated the general case of n consecutive unimolecular actions, and has plotted series of curves for the special cases $X \rightarrow Y \rightarrow Z$* and $X \rightarrow Y \rightleftarrows Z$. General equations for the case $X \rightleftarrows Y \rightleftarrows Z$ were given by Rakowski, but no further investigation was made.

The inquiry, of which the results are now described, was begun in 1903, at which date the majority of the solutions referred to above were not available. It was hoped that the study of the equations for the action $X \rightleftarrows Y \rightleftarrows Z$ might throw light on the question of the existence in aqueous solutions of dextrose of a substance intermediate between α- and β-glucose (compare Trans., 1903, **83**, 1314). At the request of one of us, the equations shown on p. 2642 were then worked out by Mr. H. Klugh, of the Central Technical College, for the case in which the concentration of one of the constituents is kept constant by contact with the solid. This case, so far as we are aware, has not been considered by any other investigator. The comparison of theory and experiment presented, in the case of the sugars, difficulties which were sufficiently great to prevent the utilisation at the time of the information which had been obtained; but the recent discovery of a series of inflected mutarotation curves rendered urgent the study of the commoner case in which the sum of the concentrations is constant, and led to the detailed inquiry recorded below.

Previous investigators have shown that under certain conditions the intermediate substance Y increases to a maximum concentration and then decreases again, whilst the concentration of the final product Z gives rise to an inflected curve when plotted against t. Our own inquiry has included the study of the intermediate substance, but special attention has been paid to the inflected curves for the final product, and a method has been devised whereby these curves may be characterised readily by drawing or calculating the intercepts of the stationary tangent on the lines which indicate the initial and final concentrations of the product.

General Solution. Case I.

If the concentrations of the three substances X, Y, and Z be represented by x, y, and z, and the four velocity constants by k_1, k_2, k_3, k_4, as shown in the scheme :

$$X \underset{k_2}{\overset{k_1}{\rightleftarrows}} Y \underset{k_4}{\overset{k_3}{\leftrightarrows}} Z,$$

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* Compare Walker, *Zeitsch. physikal. Chem.*, 1899, **28**, 177.

the fundamental equations are:

$$\frac{dx}{dt} = -k_1x + k_2y$$

$$\frac{dy}{dt} = +k_1x - (k_2 + k_4)y + k_3z$$

$$\frac{dz}{dt} = -k_3z + k_4y.$$

In the case of unsaturated solutions in which the total concentration is constant: $x + y + z = \text{const.} = 1$, the constant being taken as unity in order to simplify the algebraical working. The assumption has also been made that the experiments are carried out with materials initially homogeneous, so that when $t=0$, $x=1$, $y=0$, $z=0$, and in addition $dz/dt=0$.

The solution of the differential equations is as follows:

$$x = x_\infty\left\{-\frac{m_2}{m_2-m_1}e^{-m_1t} + \frac{m_1}{m_2-m_1}e^{-m_2t} + 1\right\} + \frac{m_2-k_1}{m_2-m_1}e^{-m_1t} + \frac{k_1-m_1}{m_2-m_1}e^{-m_2t}$$

$$y = y_\infty\left\{-\frac{m_2}{m_2-m_1}e^{-m_1t} + \frac{m_1}{m_2-m_1}e^{-m_2t} + 1\right\} + \frac{k_1}{m_2-m_1}\left\{e^{-m_1t} - e^{-m_2t}\right\}$$

$$= y_\infty\left\{-\frac{m_2(k_3-m_1)}{k_3(m_2-m_1)}e^{-m_1t} + \frac{m_1(k_3-m_2)}{k_3(m_2-m_1)}e^{-m_2t} + 1\right\}$$

$$z = z_\infty\left\{-\frac{m_2}{m_2-m_1}e^{-m_1t} + \frac{m_1}{m_2-m_1}e^{-m_2t} + 1\right\}$$

where:

$$x_\infty = \frac{k_2k_3}{k_2k_3 + k_1k_3 + k_1k_4}$$

$$y_\infty = \frac{k_1k_3}{k_2k_3 + k_1k_3 + k_1k_4}$$

$$z_\infty = \frac{k_1k_4}{k_2k_3 + k_1k_3 + k_1k_4}$$

$$m_1 = \tfrac{1}{2}\{(k_1 + k_2 + k_3 + k_4) - \sqrt{(k_1 + k_2 + k_3 + k_4)^2 - 4(k_2k_3 + k_1k_3 + k_1k_4)}\},$$

$$m_2 = \tfrac{1}{2}\{(k_1 + k_2 + k_3 + k_4) + \sqrt{(k_1 + k_2 + k_3 + k_4)^2 - 4(k_2k_3 + k_1k_3 + k_1k_4)}\},$$

$$m_1m_2 = k_2k_3 + k_1k_3 + k_1k_4.$$

These functions undergo a remarkable simplification when one or more of the velocity constants is reduced to zero. Thus, if the first stage of the action is non-reversible, $k_2 = 0$, and the m functions are reduced to the simple form:

$$m_1 = k_1;\ m_2 = k_3 + k_4;$$

if the second stage of the action is non-reversible, $k_4 = 0$, and

$$m_1 = k_1 + k_2;\ m_2 = k_3;$$

if both stages are non-reversible, $k_2 = k_4 = 0$, and

$$m_1 = k_1;\ m_2 = k_3,$$

or vice versa.

Under these conditions, the original equations can be given in terms of the velocity constants without making use of m_1 and m_2. But the simplified equations, as investigated by Mellor, by Bevan, and by Rakowski, are of very little value in the study of dynamic isomerism, since they can only be applied to non-reversible isomeric changes, and are inapplicable in all those cases in which the original substance can be recovered from its solutions by recrystallisation. We have therefore been obliged to devote our attention to discovering exactly how much information can be obtained from the study of the experimental curves in the general case in which both actions are reversible and all the four constants are finite and unknown.

Form of the yt *Curves.* Case I.

The chief feature of the *yt* curves is the occurrence under some conditions of a maximum concentration, followed by a decrease to the limiting value y_∞. The condition $dy/dt = 0$ gives for the co-ordinates of the maximum the values:

$$t_m = \frac{1}{m_2 - m_1}\log_e\frac{m_2 - k_3}{m_1 - k_3},$$

$$\frac{y_m}{y_\infty} = 1 + \frac{m_2 - k_3}{k_3}\left(\frac{m_2 - k_3}{m_1 - k_3}\right)^{\frac{-m_2}{m_2 - m_1}}.$$

If k_3 lies between m_1 and m_2, the ratio $\frac{m_2 - k_3}{m_1 - k_3}$ is negative and the logarithm imaginary; the *yt* curve then runs up steadily from the origin to the limiting value without passing through an intermediate maximum.

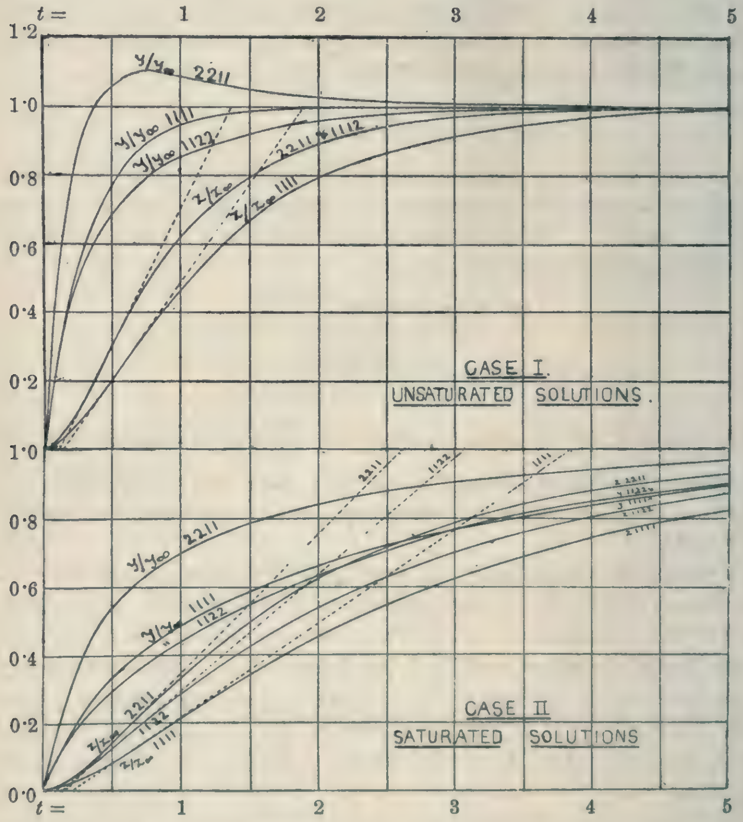
A maximum would occur if k_3 were greater than m_2 or less than m_1. The former condition we have proved to be impossible. As regards the relative magnitudes of k_3 and m_1, we have found that when k_3 is equal to m_1, $k_3 = k_1 = m_1$, whilst $k_3 \gtrless m_1$ gives $k_3 \gtrless k_1$. The occurrence of a maximum in the *yt* curve thus depends only on the relative magnitude of k_3 and k_1; if $k_3 > k_1$, no maximum can be developed whatever values are assigned to k_3 and k_4, whilst if $k_3 < k_1$, a maximum always appears.

It is noteworthy that when $k_3 = k_1$, the $e^{-m_1 t}$ factor of the *yt* equation vanishes and the curve assumes the simple logarithmic form characteristic of a single unimolecular action.

The dependence of the form of the *yt* curve on the constants k_1 and k_3, and the small influence of the constants k_2 and k_4, naturally extend to the simpler cases in which k_2 or $k_4 = 0$; they were pointed out by Rakowski as applying under these conditions, but the general case had not been investigated previously.

Form of the zt *Curves.* Case I.

The curves connecting z and t are characterised by an initial "period of induction," when $\frac{dz}{dt} = 0$, and by a point of inflexion where $\frac{d^2z}{dt^2} = 0$. In dealing with an experimental curve, the existence of a true period of induction may be demonstrated by the constancy of the initial values of z, but its duration is merely a question of the period which elapses before the sensitiveness of the methods of measurements allows of the detection of the gradual change in these values and has no quantitative value whatever. The inflexion has, however, definite quantitative features which may be recognised readily in the experimental curves. Of these, we attach special importance to two features which are independent of the actual velocity of change, a point of some importance in dealing with changes which depend on



the presence of a catalyst or impurity, and proceed with different velocities in the case of samples of different degrees of purity. These features are the co-ordinate z_i of the point of inflexion, especially when expressed by the ratio z_i/z_∞ and the ratio t_a/t_b of the intercepts t_a and t_b of the stationary tangent upon the lines $z=0$ and $z=z_\infty$.

The condition $\frac{d^2z}{dt^2}=0$ gives for the point of inflexion the co-ordinates:

$$t_i = \frac{1}{m_2 - m_1}\log_e\frac{m_2}{m_1},$$

$$\frac{z_i}{z_\infty} = -\frac{m_2}{m_2 - m_1}\left(\frac{m_2}{m_1}\right)^{\frac{-m_1}{m_2-m_1}} + \frac{m_1}{m_2 - m_1}\left(\frac{m_2}{m_1}\right)^{\frac{-m_2}{m_2-m_1}} + 1$$

$$= 1 - \frac{m_2 + m_1}{m_1}\left(\frac{m_2}{m_1}\right)^{\frac{-m_2}{m_2-m_1}}.$$

Unlike the co-ordinates for the maximum in the *yt* curve, these expressions are always real, and the point of inflexion is a regular feature of all the *zt* curves.

The tangent at the point of inflexion is given by the equation:

$$z - z_i = m(t - t_i),$$

where

$$m = z_\infty\frac{m_1m_2}{m_2 - m_1}\{e^{-m_1t_i} - e^{-m_2t_i}\}$$

$$= z_\infty m_2\left(\frac{m_2}{m_1}\right)^{\frac{-m_2}{m_2-m_1}}.$$

The intercepts, obtained by substituting $z=0$ and $z=z_\infty$ in the above equation, are given by

$$t_a = t_i - z_1/m$$

$$t_b = t_i + (z_\infty - z_i)/m.$$

The intercept-ratio is then found by substitution to be

$$\frac{t_a}{t_b} = 1 - \left(\frac{m_2}{m_1}\right)^{\frac{m_2}{m_2-m_1}} \Big/ \left\{\frac{m_2}{m_2 - m_1}\log_e\frac{m_2}{m_1} + \frac{m_2 + m_1}{m_1}\right\}.$$

It will be noticed that the ratios z_i/z_∞ and t_a/t_b depend directly on the ratio m_2/m_1, but that none of the individual velocity constants are present in the formulæ by which the values of these ratios are determined. The experimental study of the *zt* curves can therefore be used to determine the ratio m_2/m_1, but is only indirectly of value in determining the magnitudes of the individual velocity constants. The expressions which give the ratios z_i/z_∞ and t_a/t_b in terms of m_1 and m_2 are too complex to be solved easily, even when the numerical values of these ratios are known; we have therefore calculated the following table, from which the values of m_2/m_1 corresponding with any given values of z_i/z_∞ and t_a/t_b may be determined by interpolation:

TABLE I.

m_2/m_1 or m_4/m_3	z_i/z_∞	t_a/t_b
6·0	0·185	0·0607
5·0	0·198	0·0667
4·0	0·213	0·0720
3·0	0·230	0·0800
2·5	0·240	0·0841
2·0	0·250	0·0881
1·4	0·261	0·0924
1·2	0·263	0·0934
1·1	0·264	0·0938
1·0	0·264	0·0939

The limiting values, when $m_2/m_1 = 1$, are

$$\frac{z_i}{z_\infty} = 1 - \frac{2}{e} = 0·264,$$

$$\frac{t_a}{t_b} = 1 - \frac{e}{3} = 0·0939\,;$$

it follows, therefore, that if an experimental curve gives values in excess of these figures it cannot be due to two successive unimolecular changes, but probably depends on some more complex sequence.

Having determined the ratio m_2/m_1 from the ratios z_i/z_∞ and t_a/t_b, it would be easy to deduce from $t_i = \dfrac{1}{m_2 - m_1}\log_e\dfrac{m_2}{m_1}$ the individual values of m_2 and m_1, but these would probably be found to vary widely according to the amount of catalyst or impurity present in the experimental material; it is for this reason that we have laid special emphasis on determining the ratio m_2/m_1 and the ratios $k_1 : k_2 : k_3 : k_4$, rather than the absolute values of these quantities. As a trace of catalyst cannot alter the character of the final equilibrium, the ratios k_2/k_2 and k_3/k_4 must be independent of the speed of the action; a similar statement would probably be true of the ratios $k_1/k_2 : k_3/k_4$ and m_2/m_1 if the quantity, and not the nature, of the catalyst were changed, but an alteration in the relative speeds of the two stages of the action might be produced if a different catalyst were introduced into the system.

Transposition of Constants. Case I.

On examining the equations given above, it will be seen that the equations connecting z and t, as well as the equations for the co-ordinates of the point of inflexion and for the stationary tangent, do not contain any of the individual velocity constants, except in so far as these serve to determine the values of m_1, m_2, and z_∞. It therefore follows that when z/z_∞ is plotted against t, the course of the curve is determined entirely and exclusively by the values of m_1 and m_2. From this fact some important conclusions may be drawn.

1. *The* m *functions are symmetrical in reference to k_1k_2 and k_3k_4.* It is therefore possible to interchange k_1 and k_2 with k_3 and k_4 without altering in the slightest the course of the zt curve. Thus:

(*a*) On comparing the three equilibria

$$1 \underset{2}{\overset{2}{\rightleftarrows}} 1 \underset{1}{\overset{1}{\leftrightarrows}} 1 \qquad 1 \underset{1}{\overset{1}{\rightleftarrows}} 1 \underset{1}{\overset{1}{\leftrightarrows}} 1 \qquad 1 \underset{1}{\overset{1}{\rightleftarrows}} 1 \underset{2}{\overset{2}{\leftrightarrows}} 1^*,$$

in which the final proportions are the same throughout, but the relative velocity of the two changes is altered, it is noteworthy that the first and third give identical curves for z and t, although these differ widely from the curve for the second equilibrium; the three yt curves (which involve k_1) are also entirely different from one another.

(*b*) In the case of the equilibria:

$$2 \underset{2}{\overset{1}{\rightleftarrows}} 1 \underset{1}{\overset{1}{\leftrightarrows}} 1 \qquad\qquad 1 \underset{1}{\overset{1}{\rightleftarrows}} 1 \underset{2}{\overset{1}{\leftrightarrows}} 2$$

$$1 \underset{1}{\overset{2}{\rightleftarrows}} 2 \underset{1}{\overset{1}{\leftrightarrows}} 2 \qquad\qquad 2 \underset{1}{\overset{1}{\rightleftarrows}} 2 \underset{1}{\overset{2}{\leftrightarrows}} 1$$

$$1 \underset{1}{\overset{2}{\rightleftarrows}} 2 \underset{2}{\overset{1}{\leftrightarrows}} 4 \qquad\qquad 4 \underset{2}{\overset{1}{\rightleftarrows}} 2 \underset{1}{\overset{2}{\leftrightarrows}} 1$$

the form of the curve obtained by plotting z/z_∞ against t is in every respect precisely the same for the two members of each pair, in spite of the alterations which are produced in the values of z_∞ by the transposition of the constants. It is a noteworthy contrast that the alteration of relative velocities on passing from

$$2 \underset{1}{\overset{0{\cdot}5}{\rightleftarrows}} 1 \underset{1}{\overset{1}{\leftrightarrows}} 1 \text{ to } 2 \underset{2}{\overset{1}{\rightleftarrows}} 1 \underset{1}{\overset{1}{\rightleftarrows}} 1$$

alters completely the form of the zt curve, in spite of the fact that the ultimate proportions of the three isomerides remain unchanged.

2. *If $k_1 = k_3$ the* m *functions contain the other two velocity constants only in the form $k_2 + k_4$.* It is therefore possible to increase k_2 at the expense of k_4, or vice versa, without affecting in the slightest the form of the curve for z/z_∞ against t. Identical curves are therefore given by the equilibria:

$$3 \underset{3}{\overset{2}{\rightleftarrows}} 2 \underset{1}{\overset{2}{\leftrightarrows}} 1 \qquad 2 \underset{2}{\overset{2}{\rightleftarrows}} 2 \underset{2}{\overset{2}{\leftrightarrows}} 2 \qquad 1 \underset{1}{\overset{2}{\rightleftarrows}} 2 \underset{3}{\overset{2}{\leftrightarrows}} 3 \qquad 0 \underset{0}{\overset{2}{\rightleftarrows}} 2 \underset{4}{\overset{2}{\leftrightarrows}} 4,$$

in which the equilibrium is gradually displaced in favour of Z at the expense of X, until X disappears altogether, owing to the non-reversibility of the change $X \longrightarrow Y$.

Even more remarkable is the fact that when $k_1 = k_3$, the above transformation can be made without affecting the form of yt curve, which remains unaltered (for instance) over the whole range from

$$4 \underset{4}{\overset{2}{\rightleftarrows}} 2 \underset{0}{\overset{2}{\leftrightarrows}} 0 \quad \text{to} \quad 0 \underset{0}{\overset{2}{\rightleftarrows}} 2 \underset{2}{\overset{2}{\leftrightarrows}} 4.$$

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* The final proportions of x, y, and z are here shown by simple integers, for example, 1 : 1 : 1, instead of the actual values, 0·33 : 0·33 : 0·33 of $x_\infty : y_\infty : z_\infty$.

In the former limiting case the third isomeride Z is not formed at all since $k_4 = o$; the yt curve has therefore the simple unimolecular form, and this form is retained throughout the whole series of equilibria. It is noteworthy that the above transformation leaves the yt curves unaltered, and not merely the curves for y/y_∞ against t, y_∞ (unlike z_∞) remaining constant in value throughout.

General Solution. Case II.

The fundamental equations for a saturated solution in which the concentration of the original substance is kept constant by contact with the solid are:

$$x = 1 \quad \frac{dy}{dt} = k_1 - (k_2 + k_4)y + k_3 z$$

$$\frac{dz}{dt} = k_4 y - k_3 z,$$

the initial concentration being taken again as unity in order to simplify the algebraical working.

The general solution is:

$$x=1 \quad y = y_\infty \left\{ -\frac{m_4 - k_2}{m_4 - m_3} e^{-m_3 t} - \frac{k_2 - m_3}{m_4 - m_3} e^{-m_4 t} + 1 \right\}$$

$$z = z_\infty \left\{ -\frac{m_4}{m_4 - m_3} e^{-m_3 t} + \frac{m_3}{m_4 - m_3} e^{-m_4 t} + 1 \right\}$$

where

$$y_\infty = \frac{k_1}{k_2}; \quad z_\infty = \frac{k_1 k_4}{k_2 k_3},$$

$$m_3 = \tfrac{1}{2}\{(k_2 + k_3 + k_4) - \sqrt{(k_2 + k_3 + k_4)^2 - 4k_2 k_3}\},$$

$$m_4 = \tfrac{1}{2}\{(k_2 + k_3 + k_4) + \sqrt{(k_2 + k_3 + k_4)^2 - 4k_2 k_3}\},$$

$$m_3 m_4 = k_2 k_3.$$

Form of the Curves. Case II.

The condition, $dy/dt = 0$, for a maximum in the yt curve leads in this case to the equation:

$$t_{\text{max.}} = \frac{1}{m_2 - m_1} \log_e \frac{k_2 - m_4}{k_2 - m_3}.$$

The logarithm is imaginary if k_2 lies between m_4 and m_3. This, we find, must always be the case: the development of a maximum in the yt curve is therefore impossible, whatever values may be assigned to the velocity constants.

The equation for the zt curve is remarkable in that it has precisely the same form as in Case I, the only difference being that the limiting value, z_∞, and the m functions, m_3 and m_4, are derived in a different way from the velocity constants k_1, k_2, k_3, and k_4. The difference can be expressed very simply by taking the expressions for the unsaturated solution of Case I and making $k_1 = 0$ in order to convert m_1 and m_2 into m_3 and m_4, but this transformation has no experimental significance, as

k_1 appears in the expression for z_∞. It is, however, important to notice that the ratio m_4/m_3 may be determined from the experimental values of z_i/z_∞ and t_a/t_b for a saturated solution by the same equations and formulæ that were used to deduce m_2/m_1 in the case of an unsaturated solution, the table on p. 2640 being equally applicable in either case. The alteration in the form of the m functions has the effect of rendering them unsymmetrical in reference to k_1 and k_2 and k_3 and k_4; as a consequence of this alteration an interchange in the relative velocities of the two stages of the action cannot be made without altering the form of the zt curve.

Transposition of Constants. Case II.

The most important transformations in Case II are as follows:

1. *The* m *functions do not contain* k_1; moreover, this constant enters into the equations for yt and zt only as determining the values of y_∞ and z_∞. The curves for y/y_∞ against t, and for z/z_∞ against t, are therefore entirely independent of k_1. Identical curves are thus given by the equilibria:

$$2 \underset{1}{\overset{0\cdot5}{\rightleftarrows}} 1 \underset{1}{\overset{1}{\leftrightarrows}} 1 \qquad 1 \underset{1}{\overset{1}{\rightleftarrows}} 1 \underset{1}{\overset{1}{\leftrightarrows}} 1 \qquad \tfrac{1}{2} \underset{1}{\overset{2}{\rightleftarrows}} 1 \underset{1}{\overset{1}{\leftrightarrows}} 1,$$

and so on, up to the limiting case when k_1 has a very high value and the action becomes non-reversible.

2. *The* m *functions are symmetrical in reference to* k_2 *and* k_3. These constants can therefore be interchanged without affecting the form of the zt curves, the value of z_∞ being unaffected by the transposition. Identical zt curves are therefore given by the four equilibria:

$$2 \underset{2}{\overset{1}{\rightleftarrows}} 1 \underset{1}{\overset{1}{\leftrightarrows}} 1 \qquad 2 \underset{1}{\overset{1}{\rightleftarrows}} 2 \underset{1}{\overset{2}{\leftrightarrows}} 1 \qquad 1 \underset{2}{\overset{2}{\rightleftarrows}} 1 \underset{1}{\overset{1}{\leftrightarrows}} 1 \qquad 1 \underset{1}{\overset{2}{\rightleftarrows}} 2 \underset{1}{\overset{2}{\leftrightarrows}} 1,$$

the identity of the first pair with the second pair being established by means of the first transformation. This second transformation cannot be effected in the case of the yt curves, which depend in a special way on the value of k_2.

Numerical Values.

In order to illustrate the form of the curves, values have been worked out for y and z against t in the case of the three equilibria:

$$1 \underset{2}{\overset{2}{\rightleftarrows}} 1 \underset{1}{\overset{1}{\leftrightarrows}} 1 \qquad 1 \underset{1}{\overset{1}{\rightleftarrows}} 1 \underset{1}{\overset{1}{\leftrightarrows}} 1 \qquad 1 \underset{1}{\overset{1}{\rightleftarrows}} 1 \underset{2}{\overset{2}{\leftrightarrows}} 1$$

both for unsaturated solutions $(x+y+z=1)$ and for saturated solutions $(x=1)$. It will be noticed that the final equilibrium is the same throughout, but that there is an increase in the velocity of the first or of the second stage of the action in the first and last cases.

Case I.—In considering the unsaturated solutions one of the most notable features is the maximum in the yt curve when the velocity constants are 2211, the first stage proceeding twice as rapidly as the second. When the two stages are equally rapid, the curve, for constants 1111, is of the simple unimolecular type. When the constants are 1122, the growth of y is checked by the increased velocity with which it passes into z, and the curve falls below the preceding one of unimolecular type. The zt curves show the usual "period of induction" or horizontal tangent at the origin, and also exhibit points of inflexion; it is noteworthy that the curve becomes more inflected if the two stages are made to proceed with unequal velocities, but that identical effects are produced by accelerating either the first or the second stage of the action; doubling the velocity of either stage raises the point of inflexion from 21·7 to 23·0 per cent. of the final value, and increases the ratio of the intercepts of the stationary tangent from 0·075 to 0·080.

Case II.—The six curves that are plotted for saturated solutions call for but little comment. Two of the yt curves, those for constants 1111 and 1122, intersect at $t=3$ (approx.), in addition to being coincident at the origin, $t=0$, and at $t=\infty$. The zt curves are all distinct, the inflected character of the curve being increased by accelerating the first, and decreased by accelerating the second, stage of the action, the ordinate of the point of inflexion being changed from 0·175 to 0·187 and 0·146 respectively, whilst the intercept ratio, 0·058, is increased to 0·062 in the former, and decreased to 0·045 in the latter, case.

TABLE II. *Numerical Values.*

	Case I.						Case II.					
	y/y_∞.			z/z_∞.			y/y_∞.			z/z_∞.		
t.	2211.	1111.	1122.	2211.	1111.	1122.	2211.	1111.	1122.	2211.	1111.	1122.
0·1	0·471	0·259	0·248	0·025	0·013	Same as 2211.	0·173	0·091	0·087	0·009	0·005	0·009
0·2	0·753	0·451	0·418	0·082	0·046		0·303	0·166	0·154	0·055	0·016	0·029
0·4	1·014	0·699	0·624	0·232	0·155		0·478	0·282	0·254	0·098	0·055	0·089
0·6	1·091	0·835	0·737	0·383	0·260		0·584	0·367	0·328	0·177	0·104	0·156
0·8	1·102	0·909	0·807	0·512	0·356		0·654	0·433	0·388	0·258	0·158	0·224
1·0	1·091	0·950	0·855	0·619	0·473		0·705	0·486	0·441	0·335	0·213	0·287
1·2	1·075	0·973	0·889	0·703	0·562		0·744	0·531	0·489	0·406	0·267	0·347
1·4	1·060	0·985	0·915	0·769	0·638		0·776	0·569	0·532	0·470	0·319	0·401
1·6	1·047	0·992	0·934	0·821	0·701		0·802	0·603	0·572	0·528	0·367	0·451
1·8	1·037	0·995	0·949	0·861	0·754		0·825	0·634	0·608	0·580	0·413	0·497
2·0	1·029	0·998	0·960	0·892	0·798		0·845	0·662	0·641	0·626	0·455	0·540
2·5	1·015	0·999	0·979	0·943	0·877		0·884	0·726	0·711	0·721	0·550	0·630
3·0	1·008	1·000	0·989	0·970	0·925		0·914	0·770	0·768	0·792	0·636	0·703
4·0	1·002	—	0·997	0·991	0·972		0·952	0·843	0·850	0·884	0·746	0·808
5·0	1·001	—	0·999	0·998	0·990		0·973	0·893	0·904	0·935	0·827	0·876
10·0	1·000	—	1·000	1·000	1·000		0·999	0·984	0·990	0·997	0·974	0·986
t_m or t_i	0·778	No	No	0·549	0·380		No	No	No	0·623	0·861	0·569
$\frac{y_m}{y_\infty}$ or $\frac{z_i}{z_\infty}$	1·102	max.	max.	0·230	0·217		max.	max.	max.	0·187	0·175	0·146
t_a	—	—	—	0·151	0·103		—	—	—	0·164	0·225	0·140
t_b	—	—	—	1·883	1·380		—	—	—	3·623	3·861	3·069
t_a/t_b	—	—	—	0·080	0·075		—	—	—	0·062	0·058	0·045

Summary and Conclusions.

1. Equations are given for the changes of concentration which take place in a reversible chemical action which proceeds in two stages, each obeying the unimolecular law. When the total concentration is constant the intermediate form may pass through a maximum concentration, but this is not possible when the concentration of the initial form is kept constant, for instance, by saturation with the solid. In each case, however, the growth of the third form is represented by curves which exhibit a period of induction and a point of inflexion.

2. The occurrence of a maximum concentration of the intermediate form depends exclusively on the velocities with which it is produced from the other two forms, and is independent of the velocities with which it passes into these forms.

3. The inflected curves showing the growth of the concentration of the final product are independent of the individual velocity constants, except in so far as these determine the value of certain "*m*" functions, involving in the case of unsaturated solutions all the four velocity constants, but in the case of a saturated solution only three of them. The ratio of the two "*m*" functions can be deduced from the concentration at which the point of inflexion occurs, or by drawing the stationary tangent and measuring its intercepts on the lines showing the initial and final concentrations of the product. If the concentration at the point of inflexion is greater than 26·4 per cent. of the final concentration, or if the ratio of the intercepts is greater than 0·0939, the curve cannot be due to two consecutive unimolecular actions and must depend on some more complex sequence.

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CCLXX.—*The Dinitro-derivatives of Dimethyl*-p-*toluidine*

By Gilbert T. Morgan and Arthur Clayton.

The nitration of aromatic amines under various conditions presents certain features of considerable theoretical interest in connexion with the mode in which substitution occurs in the aromatic nucleus.

In many cases it is found desirable to moderate the action of nitric acid on these bases by nitrating them in the form of their acyl derivatives, the acetyl compound being most frequently employed for this purpose. This method of nitration leads, in the great majority of cases, to the production of ortho- and para-nitro-derivatives, the substitution of the nitro-group in these conditions obeying the ortho-para law.

When, however, the benzenoid amines are nitrated in concentrated sulphuric acid, the nitro-group tends to enter a meta-position with respect to the aminic nitrogen, so that the chief product is frequently, although not invariably, a meta-nitro-derivative in conformity with the meta law of substitution. Aniline, for instance, when nitrated in excess of concentrated sulphuric acid, gives a mixture of nitro-compounds, in which *m*-nitroaniline predominates. *o*-Toluidine, under similar conditions, yields 4-nitro- and 6-nitro-*o*-toluidine, whilst *p*-toluidine furnishes 2-nitro-*p*-toluidine, these three products each having the nitro-group in a meta-position with regard to the aminic nitrogen.

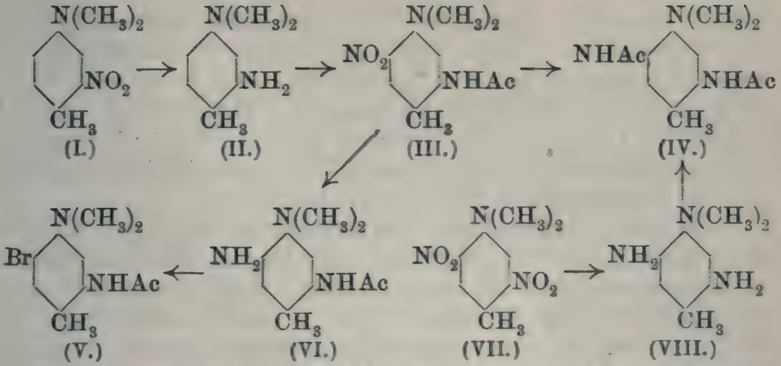
The nitration of the aromatic monoalkyl amines in concentrated sulphuric acid proceeds along similar lines, methyl-*o*-toluidine and methyl-*p*-toluidine yielding respectively 4-nitromethyl-*o*-toluidine and 2-nitromethyl-*p*-toluidine (Gnehm and Blumer, *Annalen*, 1899, **304**, 99; Pinnow, *Ber.*, 1895, **28**, 3040).

The case of the tertiary bases presents several points of interest. Dimethylaniline yields a mixture containing three to four parts of *m*-nitrodimethylaniline to one part of *p*-nitrodimethylaniline (Groll, *Ber.*, 1886, **19**, 1944). Dimethyl-*o*-toluidine and dimethyl-*p*-toluidine give rise respectively to 4-nitrodimethyl-*o*-toluidine and 2-nitrodimethyl-*p*-toluidine, in both of which the nitro-group is meta to the aminic nitrogen (Gnehm and Blumer, *loc. cit.*, p. 107, and D.R.-P. 69188).

When dimethyl-*p*-toluidine, dissolved in concentrated sulphuric acid, is treated with sufficient strong nitric acid to form di- or even tri-nitro-derivatives, the reaction nevertheless proceeds only to the extent of producing 2-nitrodimethyl-*p*-toluidine, even when the temperature of the concentrated acid solution is raised to 70°. But on pouring this acid liquid into water so that the temperature reaches 40°, further nitration occurs, with the production of a dinitrodimethyl-*p*-toluidine (m. p. 103—104°) in practically quantitative yield. This dinitro-compound is apparently identical with a by-product of the action of nitrous acid on dimethyl-*p*-toluidine (Pinnow, *Ber.*, *loc. cit.*, p. 2039).

In the present communication the constitution of this dinitro-compound has been determined in the following manner.

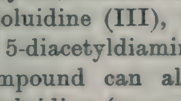
Since the compound can be prepared either directly from dimethyl-*p*-toluidine or by the further nitration of 2-nitrodimethyl-*p*-toluidine (I), it follows that one of the nitro-groups is in position 2 with respect to the methyl radicle:



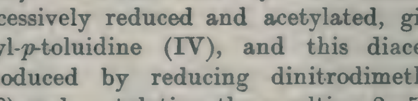
2-Nitrodimethyl-*p*-toluidine (I), on reduction, yields *as*-4-dimethyl-2 : 4-tolylenediamine (II), which, when successively acetylated and nitrated, furnishes *5-nitro-2-acetylaminodimethyl-*p*-toluidine* (III). The position of the entrant nitro-group in compound III is ascertained by reduction, when *2-acetyl-2 : 5-diaminodimethyl-*p*-toluidine* (VI) is obtained, and this triamine is converted by the Sandmeyer reaction into 5-bromo-2-acetylaminodimethyl-*p*-toluidine (V), the constitution of which has been fully established (Morgan and Clayton, Trans., 1905, **87**, 946). But 5-nitro-2-acetylaminodimethyl-*p*-toluidine (III), when successively reduced and acetylated, gives 2 : 5-diacetyldiaminodimethyl-*p*-toluidine (IV), and this diacetyl compound can also be produced by reducing dinitrodimethyl-*p*-toluidine (m. p. 103—104°) and acetylating the resulting 2 : 5-diaminodimethyl-*p*-toluidine (VIII).

These two methods of preparing the same diacetyl compound (IV) prove conclusively that the dinitro-compound melting at 103—104° is *2 : 5-dinitrodimethyl-*p*-toluidine* (VII).

Before the foregoing direct proof was worked out, an indirect method had been adopted, which consisted in preparing *2 : 6-dinitrodimethyl-*p*-toluidine* (IX) and comparing its properties with those of the above-described 2 : 5-compound. The 2 : 6-compound is prepared by reducing 2 : 4 : 6-trinitrotoluene to 2 : 6-dinitro-*p*-toluidine, and methylating this base with methyl sulphate:



(IX. M. p. 192°.)



(X. Pinnow, m. p. 95°.) (XI.)

3 : 5-Dinitrodimethyl-*p*-toluidine was prepared by Pinnow and Matcovich (*Ber.*, 1898, **31**, 2518) by the action of dilute nitric and sulphuric acids on dimethyl-*p*-toluidine, a chemical change which probably takes place in two stages, for 3-nitrodimethyl-*p*-toluidine

(XI) is formed by the action of aqueous nitrous acid on dimethyl-*p*-toluidine (Pinnow, *Ber.*, 1895, **28**, 3039). It therefore follows that the dinitro-compound melting at 103—104° must be either the 2 : 5- or 2 : 3-dinitrodimethyl-*p*-toluidine. Reduction to the triamine (VIII) showed that the compound was the 2 : 5-isomeride, since the base had all the properties of a para-diamino-compound, and did not react at all like an ortho-diamine.

These results indicate that the nitration of dimethyl-*p*-toluidine takes place in two different ways, depending on the concentration of the acid medium. In strong sulphuric acid, a meta-position to the aminic nitrogen is assumed by the entrant nitro-group, and this formation of 2-nitrodimethyl-*p*-toluidine represents the only stage of nitration so long as the acid remains concentrated. Dilution of the acid with water leads to the introduction of nitro-groups in the ortho-positions with respect to the basic nitrogen atom (compare formulæ VII, X, and XI). In strong acid, the meta-law of substitution is obeyed, whereas nitration in presence of water conforms to the ortho-para law.

These nitration phenomena may be profitably discussed in connexion with the rule put forward by Crum Brown and Gibson (Trans., 1892, **61**, 367) for determining whether a benzenoid monoderivative shall give a meta-di-derivative or a mixture of ortho- and para-di-derivatives. The rule is applied by considering the hydride of the radicle already present in the molecule, and if this hydride is directly oxidisable to the corresponding hydroxy-derivative, then substitution takes place according to the meta law. For example, the nitro-group, which determines the entry of the second radicle mainly into a meta-position, has the hydride nitrous acid, $H{\cdot}NO_2$, and this is directly oxidisable to nitric acid, $HO{\cdot}NO_2$.

On the other hand, methyl has the hydride methane, $H{\cdot}CH_3$, which is not readily oxidisable to methyl alcohol, $HO{\cdot}CH_3$. In this case the group methyl determines the entry of other radicles into ortho- and para-positions.

This generalisation, although quite empirical, is a remarkably comprehensive rule, and it may be applied successfully to several cases which had not been examined eighteen years ago, when Crum Brown and Gibson first proposed it.

The triazo group N_3 has the hydride $H{\cdot}N_3$ not directly oxidisable to a compound $HO{\cdot}N_3$, and, in accordance with the rule, N_3 induces the entry of other radicles into ortho- and para-positions.

The group AsO_3H_2 present in phenylarsinic acid has the hydride $H{\cdot}AsO_3H_2$, which is directly oxidisable to arsenic acid, $HO{\cdot}AsO_3H_2$, and in conformity with the rule this group favours substitution in meta-positions.

The primary benzenoid amines were placed by Crum Brown in the category of substances obeying the ortho-para law; this mode of substitution agreeing with the fact that the hydride $H\cdot NH_2$ is not directly oxidisable to hydroxylamine, $HO\cdot NH_2$. The generalisation can be extended to the acetyl derivatives; the hydride $H\cdot NH\cdot CO\cdot CH_3$ is not directly oxidisable to $HO\cdot NH_2\cdot CO\cdot CH_3$, which is in accordance with the fact that the nitration of acetyl derivatives generally follows the ortho-para law.

When, however, the bases are nitrated in strong sulphuric acid, one must consider the group $NH_2\cdot H_2SO_4$ having the hydride $H\cdot NH_2\cdot H_2SO_4$, which is not directly oxidisable to $HO\cdot NH_2\cdot H_2SO_4$. In accordance with the Crum Brown and Gibson rule, the presence of this sulphate group should lead to the formation of ortho-para-derivatives, but in many cases substitution occurs by preference in the meta-position. Aniline and dimethylaniline each give products in which the meta-nitro-derivative predominates.

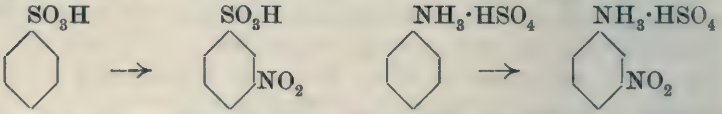
The case of the tertiary bases is of especial interest, because it may be argued that, under certain conditions, the hydride $H\cdot NR_2$ is directly oxidisable to $HO\cdot NR_2$; thus diethylamine with hydrogen peroxide yields diethylhydroxylamine (Dunstan and Goulding, Trans., 1899, **75**, 1009), and dimethylaniline itself can be oxidised to dimethylaniline oxide. Yet, strangely enough, in dilute solutions, where these tertiary amines may be supposed to be reacting partly in the free state, they nitrate in accordance with the ortho-para law, and only in combination with concentrated sulphuric acid do they react in conformity with the meta law.

In whichever way the tertiary amines are nitrated, whether in strong or dilute acid, there is a discrepancy between the facts and the application of the Crum Brown and Gibson rule to these phenomena. While indicating this limitation to a rule which has proved fairly general, the authors do not wish to put forward a theory sufficiently comprehensive to include all cases of the nitration of aromatic amines, but they suggest as a working hypothesis that the nitration of an aromatic base or its acetyl derivative is a process essentially different from the nitration of the sulphate of the base in concentrated sulphuric acid (compare Armstrong, Trans., 1887, **51**, 589).

In the former case, the nitric acid is attracted first to the amino- or the acetylamino-group, giving rise to a nitrate by direct addition; dehydration leads to the production of a nitroamine, and then follows substitution in the sympathetic ortho- and para-positions.

In the latter method of nitration the radicle $\cdot NH_3\cdot HSO_4$, $\cdot NH_2R\cdot HSO_4$, or $\cdot NHR_2\cdot HSO_4$ acts as a strongly acidic group, which, so far from attracting the nitric acid, actually exerts a slight but appreciable repulsive action, so that the introduction of the nitro-group takes place in the apathetic meta-position, this being shielded from the direct influence of the aminosulphate complex.

The process is comparable to the nitration of a sulphonic acid:



and in both instances the meta-derivatives predominate (compare Flürscheim, *J. pr. Chem.*, 1902, [ii], **66**, 324).

This view of the nitration of aromatic amines in concentrated sulphuric acid affords an explanation of the course of substitution in the naphthalene as well as in the benzene series.

EXPERIMENTAL.

Nitration of Dimethyl-p-*toluidine.*

Dimethyl-*p*-toluidine, dissolved in twelve parts of cold concentrated sulphuric acid and treated with two to three molecular proportions of nitric acid also dissolved in strong sulphuric acid, underwent nitration only to the extent of forming 2-nitrodimethyl-*p*-toluidine (m. p. 37°), for this base separated in practically quantitative yield when the acid solution was poured into ice-cold water or dilute aqueous ammonia.

The nitration proceeded no further than the formation of the mononitro-compound, even when excess of fuming sulphuric and nitric acids were employed at 70°. At higher temperatures, sulphonation and even destructive oxidation set in, but no higher nitro-compounds could be detected.

When, however, the solution of 2-nitrodimethyl-*p*-toluidine in concentrated sulphuric acid, and one molecular proportion of nitric acid was poured into four volumes of water, so that the temperature rose to 40°, further nitration occurred, with the production of 2:5-*dinitrodimethyl*-p-*toluidine* (m. p. 103—104°), the yield being practically quantitative:

0·1650 gave 0·2872 CO_2 and 0·0742 H_2O. $C=47{\cdot}45$; $H=5{\cdot}00$.

$C_9H_{11}O_4N_3$ requires $C=47{\cdot}99$; $H=4{\cdot}89$ per cent.

2:5-Dinitrodimethyl-*p*-toluidine (VII) can also be prepared by dissolving 2-nitrodimethyl-*p*-toluidine in concentrated nitric and sulphuric acids, and pouring the solution into four volumes of water.

5-*Nitro-2-acetylaminodimethyl*-p-*toluidine* (III).

2-Nitrodimethyl-*p*-toluidine was reduced with tin and hydrochloric acid (Trans., 1905, **87**, 948), and the resulting 2-aminodimethyl-*p*-toluidine acetylated.

2-Acetylaminodimethyl-*p*-toluidine was dissolved in 10 parts of cold concentrated sulphuric acid, and treated with about half its weight of nitric acid (sp. gr. 1·4), diluted with three volumes of strong sulphuric acid. No reaction occurred in the strong acid, but on pouring the solution into water, so that the temperature rose to 70°, nitration set in, and on adding dilute ammonia, *5-nitro-2-acetylaminodimethyl-*p*-toluidine* separated, and was crystallised from alcohol, yielding yellow needles, melting at 155°:

0·1272 gave 0·2594 CO_2 and 0·0768 H_2O. C = 55·61; H = 6·71.
0·1229 „ 19·0 c.c. N_2 at 18° and 760 mm. N = 17·85.
$C_{11}H_{15}O_3N_3$ requires C = 55·69; H = 6·32; N = 17·72 per cent.

*2-Acetyl-2 : 5-diaminodimethyl-*p*-toluidine* (VI).

The foregoing nitroacetyl compound underwent simultaneous reduction and hydrolysis on treatment with tin and hydrochloric acid, and was accordingly reduced with iron filings and water slightly acidified with acetic acid, the reducing agent being slowly added to the boiling solution until the colour disappeared. The solution, after neutralisation with sodium carbonate and filtration, was evaporated to dryness, and the residue, when dissolved in water, crystallised therefrom in colourless crystals, melting at 131—133°:

0·1056 gave 18·2 c.c. N_2 at 16° and 759 mm. N = 20·06.
$C_{11}H_{17}ON_3$ requires N = 20·28 per cent.

*2-Acetyl-2 : 5-diaminodimethyl-*p*-toluidine* was dissolved in hydrobromic acid containing cuprous chloride, the solution warmed to 80°, and slowly treated with aqueous sodium nitrite (1 mol.). The cooled liquid was rendered ammoniacal, and the precipitate crystallised from alcohol, when it separated in colourless, woolly needles, melting at 163°, and was identified by the method of mixed melting points as 5-bromo-2-acetylaminodimethyl-*p*-toluidine (V), the constitution of which has already been determined (Trans., 1905, **87**, 948).

*2 : 5-Diaminodimethyl-*p*-toluidine* (VIII) (compare Pinnow and Matcovich, *loc. cit.*).—Granulated tin was added to a hot solution of 24 grams of 2 : 5-dinitrodimethyl-*p*-toluidine in 150 c.c. of concentrated hydrochloric acid and 50 c.c. of water until the colour disappeared. After removing the tin as sulphide, the filtrate was evaporated until 2 : 5-diaminodimethyl-*p*-toluidine hydrochloride separated in colourless crystals. The base set free by ammonia was extracted with chloroform, and on evaporating off the solvent from the carefully dried extract, the triamine was left as an oil, which rapidly oxidised on exposure to the atmosphere and solidified on cooling.

*2 : 5-Diacetyldiaminodimethyl-*p*-toluidine* (IV), obtained by treating the preceding base with acetic anhydride, crystallised from very dilute alcohol in colourless needles, and after repeated crystallisation softened at 233°, and melted at 236°. (Found, N = 16·99. Calc., N = 16·86 per cent.)

When heated at 245° for thirty minutes, this diacetyl compound remained unchanged, showing that it was not an ortho-diacetylated compound.

When used in the form of its hydrochloride, 2 : 5-diaminodimethyl-*p*-toluidine gave the colour reactions of a para-diamine. Oxidation with chromic acid, either alone or in presence of aniline, gave a deep red coloration, indicating the production of a safranine dye. Alkaline hypochlorite, in presence of α-naphthol, led to the production of a blue indophenol. When heated in alcoholic acetic acid solution with phenanthraquinone and sodium acetate, no azine condensation occurred. The triamine underwent diazotisation in acid solution, and the product coupled with alkaline β-naphthol, yielding an azo-derivative. These reactions afforded additional evidence that the triamine has the constitution (VIII) assigned to it on p. 2647. A final confirmation was obtained by preparing 2 : 5-diacetyldiaminodimethyl-*p*-toluidine by an alternative method, using 2-acetyl-2 : 5-diaminodimethyl-*p*-toluidine (VI), since the latter compound has been shown to contain its free amino-group in position 5.

2 : 6-*Dinitrodimethyl*-p-*toluidine* (IX).

2 : 6-Dinitro-*p*-toluidine, prepared by reducing 2 : 4 : 6-trinitrotoluene with alcoholic ammonium sulphide (Holleman and Böeseken, *Rec. trav. chim.*, 1897, **16**, 425), was slowly added to methyl sulphate at 160—165°, and the solution maintained at this temperature for thirty minutes. The liquid was then rendered alkaline with sodium hydroxide, and the solid product crystallised from 50 per cent. acetic acid:

0·1307 gave 0·2290 CO_2 and 0·0614 H_2O. C = 47·79; H = 5·21.

0·1344 „ 22·2 c.c. N_2 at 23° and 756 mm. N = 18·52.

$C_9H_{11}O_4N_3$ requires C = 47·99; H = 4·89; N = 18·66 per cent.

2 : 6-*Dinitrodimethyl*-p-*toluidine* separates in yellow needles, melting at 192°.

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Yeast cells, the rôle of diffusion in fermentation by (SLATOR and SAND), T., 922; P., 85; (BROWN), P., 30.

FORMULA INDEX.

The following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 group, C_2 group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Simple metallic salts of acids are indexed under the respective acids.

Simple salts of bases (for example, hydrochlorides, platinichlorides, and picrates), when described for the purpose of further identifying the base, are indexed under the latter.

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CO Carbon monoxide, effect of temperature on the dissociation equilibrium of (Rhead and Wheeler), T., 2178; P., 220.

CO_2 Carbon dioxide, absorption of, by *p*-azoxyphenetole, relation between solubility and the physical state of the solvent in the (Homfray), T., 1669; P., 197.

CS Carbon monosulphide, Deniger's, non-existence of (Dunn), P., 116.

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CH_2NCl Methylenechloroamine (Cross, Bevan, and Bacon), T., 2404; P., 248.

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$CH_4O_2N_2S$ Aminoiminomethanesulphinic acid (Barnett), T., 64.

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C_2H_2O Keten, some reactions of, and its combination with hydrocyanic acid (Deakin and Wilsmore), T., 1968; P., 216; polymerisation of (Chick and Wilsmore), T., 1978; P., 217.

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$C_2H_2ON_4$ Triazomethylcarbimide (Forster and Müller), T., 1061; P., 112.

$C_2H_3ON_7$ Substance, from triazomethylcarbimide and water (Forster and Müller), T., 1064.

$C_2H_3O_2Br$ Bromoacetic acid, interaction of, and its sodium salt, with silver salts in aqueous solution (Senter), T., 346; P., 23.

$C_2H_4N_3Cl$ Triazoethyl chloride (Forster and Newman), T., 2575; P., 322.

$C_2H_4N_3Br$ Triazoethyl bromide (Forster and Newman), T., 2576; P., 322.

$C_2H_4N_3I$ Triazoethyl iodide (Forster and Newman), T., 2577; P. 322.

$C_2H_5ON_5$ Triazomethyl carbamide (Forster and Müller), T., 1065; P., 113.

$C_2H_6O_4S$ Methyl sulphate, complete methylation by (Meldola), P., 232.

C_3 Group.

$C_3H_4O_4$ Malonic acid, determination of, by potassium permanganate (Cameron and McEwan), P., 144.

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$C_3H_4O_2N_8$ Bistriazomalonamide (Forster and Müller), T., 138; P., 4.

$C_3H_5O_2Br$ α-Bromopropionic acid, interaction of, and its sodium salt, with silver salts in aqueous solution (Senter), T., 346; P., 23.

$C_3H_7O_2Cl$ Glycerol α-monochlorohydrin, preparation of aryl ethers of (Boyd and Marle), T., 1788; P. 208.

C_4 Group.

$C_4H_2O_3$ Maleic anhydride, rate of hydration of (Rivett and Sidgwick), T., 1677; P., 200; action of Grignard reagents on (Purdie and Arup), T., 1537; P., 199.

C_4H_4O Furan, absorption spectrum of (Purvis), T., 1648; P., 201.

$C_4H_4O_2$ *cyclo*Butan-1:3-dione, preparation and properties of (Chick and Wilsmore), T., 1984; P., 217.

$C_4H_4O_3$ Succinic anhydride, rate of hydration of (Rivett and Sidgwick), T., 1677; P., 200.

C_4H_4S Thiophen, absorption spectrum of (Purvis), T., 1648; P., 201.

C_4H_5N Pyrrole, absorption spectrum of (Purvis), T., 1648; P., 201.

$C_4H_6O_3$ Acetic anhydride, rate of hydration of (Rivett and Sidgwick), T., 732; P., 66.

$C_4H_6O_4$ Succinic acid, sodium salts of (Marshall and Bain), T., 1074; P., 114.

$C_4H_{10}O$ Ethyl ether, physical properties of mixtures of, and sulphuric acid (Pound), P., 341; compounds of, with mercuric halides and halogen salts (Marsh), T., 2305.

Trimethylcarbinol, crycosopic. ebullioscopic and association constants of (Atkins), P., 342.

4 III

$C_4H_4N_2Br_2$ Dibromo-4(or 5)-methylglyoxaline, and its silver salts (Pyman), T., 1826; P., 212.

$C_4H_5O_4N_3$ Methyltriazomalonic acid (Forster and Müller), T., 131; P., 4.

$C_4H_5N_2Br$ Bromo-4(or 5)-methylglyoxaline, and its salts (Pyman), T., 1826; P., 212.

$C_4H_6O_2Br_2$ αβ-Dibromobutyric acid, action of bases on, and its esters (James), T., 1565 ; P., 201.

$C_4H_7O_2N_5$ Methyltriazomalonamide (Forster and Müller), T., 133 ; P., 4.

$C_4H_7O_2Br$ α-Bromobutyric acid, interaction of, and its sodium salt, with silver salts in aqueous solution (Senter), T., 346 ; P., 23.

$C_4H_8O_4N_2$ Tartramide, the influence of various substituents on the optical activity of (Frankland and Twiss), T., 154 ; P. 5.

$C_4H_8N_2S$ Allylthiocarbamide, oxidation of (Barnett), T., 65.

$C_4H_9ON_3$ β-Triazoethyl ether (Forster and Newman), T., 2579 ; P., 322.

$C_4H_9O_2N_7$ Substance from triazomethylcarbimide and ammonia (Forster and Müller), T., 1066.

4 IV

$C_4H_8O_2N_2S$ Allyl derivative of aminoiminomethanesulphinic acid ($+H_2O$) (Barnett), T., 65.

C_5 Group.

C_5H_{10} *cyclo*Pentane, formation of imino-derivatives of, from open-chain mononitriles (Mitchell and Thorpe), T., 997 ; P., 114.

5 II

$C_5H_4O_2$ Furfuraldehyde, absorption spectrum of (Purvis), T., 1648 ; P., 201.

$C_5H_4O_3$ Citraconic and itaconic anhydrides, rate of hydration of (Rivett and Sidgwick), T., 1677 ; P., 200.

C_5H_5N Pyridine, absorption spectra of the vapours of, and its derivatives (Purvis), T., 692.

$C_5H_6O_3$ Methylsuccinic anhydride, rate of hydration of (Rivett and Sidgwick), T., 1677 ; P., 200.

$C_5H_6O_4$ *l*-Methoxysuccinic anhydride (Purdie and Young), T., 1531.

$C_5H_8O_5$ *l*-Methoxysuccinic acid, silver salt of (Purdie and Neave), T., 1518.

$C_5H_8N_2$ 1:4-Dimethylglyoxaline, and its salts (Pyman), T., 1821 ; P., 212.

1:5-Dimethylgloxaline, and its salts (Pyman), T., 1823 ; P., 212.

$C_5H_9N_3$ β-Amino-4-ethylgloxaline, identity of, with base from ergot (Barger and Dale), T., 2592 ; P., 327.

$C_5H_{11}N$ Piperidine, absorption spectrum of the vapour of (Purvis), T., 705.

5 III

$C_5H_5O_2N$ α-Acetoxyacrylonitrile (Deakin and Wilsmore), T., 1969 ; P., 216.

$C_5H_6O_3Cl_2$ *l*-Methoxysuccinyl chloride (Purdie and Young), T., 1530.

$C_5H_6N_2Br_2$ 2:5-Dibromo-1:4-dimethylglyoxaline (Pyman), T., 1831.

$C_5H_7O_2Br$ Allyl bromoacetate (Clarke), T., 428.

$C_5H_7O_4N_3$ Ethyltriazomalonic acid (Forster and Müller), T., 133 ; P., 4.

$C_5H_7N_2Br$ 2 (or 5)-Bromo-1:4-dimethylglyoxaline, and its salts (Pyman), T., 1828 ; P., 212.

2(or 4)-Bromo-1:5-dimethylglyoxaline, and its salts (Pyman), T., 1829 ; P., 212.

$C_5H_8O_2Br_2$ Methyl αβ-dibromobutyrate (James), T., 1572.

$C_5H_8O_3N_4$ Tetrahydrouric acid, synthesis of (Frankland), T., 1316 ; P., 171.

$C_5H_9O_2N$ Butyryl- and *iso*butyryl-formamide, synthesis of (Barger and Ewins), T., 291 ; P., 2.

$C_5H_9O_2N_5$ Ethyltriazomalonamide (Forster and Müller), T., 134 ; P., 4.

$C_5H_9O_4N$ *l*-Methoxysuccinamic acid (Purdie and Young), T., 1532.

$C_5H_9O_4Br$ α-Bromoacetin (Alpern and Weizmann), P., 345.

$C_5H_{10}O_3N_2$ *l*-Methoxysuccindiamide (Purdie and Neave), T., 1519.

$C_5H_{10}O_4N_6$ Substance, from triazomethylcarbimide and water (Forster and Müller), T., 1063.

C_6 Group.

C_6H_6 Benzene, separation of *cyclo*hexane from mixtures containing (Patterson and Fleck), T., 1773 ; P., 207.

C_6H_{12} *cyclo*Hexane, its separation from, and estimation in, mixtures containing benzene (Patterson and Fleck), T., 1773 ; P., 207.

6 II

C_6H_6O Phenol, freezing-point curve for mixtures of camphor and (Wood and Scott), T., 1573 ; P., 194.

$C_6H_6O_2$ Resorcinol, condensation of benzaldehyde with (Pope and Howard), T., 78 ; condensation of anisaldehyde with (Pope and Howard), T., 972 ; P., 88.

$C_6H_6O_4$ Anhydride of *cis*-tetrahydrofuran-2:5-dicarboxylic acid (Le Sueur and Haas), T., 183.

C_6H_6S Phenyl mercaptan, interaction of, with thionyl chloride (Tasker and Jones), P., 234.

C_6H_7N Aniline, absorption spectra of (Purvis), T., 1546 ; P., 194 ; colorimetric measurement of hydrolysis of salts of (Tizard), T., 2490 ; P., 225.

α-Picoline, absorption spectrum of the vapour of (Purvis), T., 700.

$C_6H_8O_4$ Methyl maleate, action of Grignard reagents on (Purdie and Arup), T., 1537 ; P., 199.

$C_6H_8O_5$ *cis*-Tetrahydrofuran-2:5-dicarboxylic acid, ammonium salt of (Le Sueur and Haas), T., 183.

d-Dimethoxysuccinic anhydride (Purdie and Young), T., 1533.

$C_6H_8O_7$ Citric acid, potassium cupric salts of (Pickering), T., 1837 ; P., 17.

$C_6H_{10}O_5$ Methyl hydrogen *l*-methoxysuccinate (Purdie and Young), T., 1531.

$C_6H_{12}O$ Methyl *tert.*-butyl ketone, action of, on ketols (Boon), T., 1256 ; P., 94.

$C_6H_{12}O_6$ *d*-Fructose, acetone derivatives of (Irvine and Garrett), T., 1277 ; P., 143.

6 III

$C_6H_3O_6N_3$ *s*-Trinitrobenzene, additive compounds of, with arylamines (Sudborough and Beard), T., 773 ; P., 71.

$C_6H_3O_8N_5$ Tetranitroaniline (Flürscheim and Simon), P., 81.

$C_6H_6O_3N_{12}$ Tristriazomethyl*iso*cyanurate (Forster and Muller), T., 1064 ; P., 112.

$C_6H_8O_3N_6$ Ethyl *αα*-bistriazoacetoacetate (Forster and Newman), T., 1367; P., 197.

$C_6H_8O_4Cl_2$ *d*-Dimethoxysuccinyl chloride (Purdie and Young), T., 1532.

$C_6H_9O_3N_3$ Methyl *α*-triazomethylacetoacetate (Forster and Newman), T., 1363 ; P., 197.

$C_6H_9O_3Cl$ Methyl *α*-chloromethylacetoacetate (Forster and Newman), T., 1363.

$C_6H_{11}O_2Br$ *n*-Butyl bromoacetate (Clarke), T., 428.

tert-Butyl bromoacetate (Clarke), T., 428.

$C_6H_{12}O_3N_6$ Semicarbazone-semicarbazide of acetoacetic acid (Chick and Wilsmore), T., 1991 ; P., 217.

6 IV

$C_6H_3O_3I_3S$ 2:3-5-, 2:4:5-, and 3:4:5-Tri-iodobenzenesulphonic acid, metallic salts of (Boyle), T., 217 ; P., 4.

$C_6H_4O_3I_2S$ 2:4- and 3:5-Di-iodobenzenesulphonic acid, metallic salts of (Boyle), T., 216 ; P., 4.

C_7 Group.

C_7H_8 Toluene, chlorination of (Cohen, Dawson, Blockey and Woodmansey), T., 1623 ; P., 205.

7 II

$C_7H_4N_4$ *o*-Triazobenzonitrile (Forster and Judd), T., 262.

C_7H_6O Benzaldehyde, condensation of resorcinol with (Pope and Howard), T., 78.

C_7H_8S Benzyl mercaptan, reactions of (Smythe and Forster), T., 1195 ; P., 135.

C_7H_9N Benzylamine, absorption spectrum of (Purvis), T., 1552.

Methylaniline, absorption spectrum of (Purvis), T., 1551.

o- and *m*-Toluidine, absorption spectra of (Purvis), T., 1551.

p-Toluidine, and its condensation product with acetaldehyde, absorption spectra of (Purvis), T., 664 ; P., 56.

2:4-and 2:6-Lutidine, absorption spectra of the vapours of (Purvis), T., 702.

Δ^1-*cyclo*Penteneacetonitrile (Harding and Haworth), T., 491.

$C_7H_{10}O_2$ Δ^1-*cyclo*Penteneacetic acid, and its silver salt (Harding and Haworth), T., 491 ; P., 61.

*cyclo*Pentylideneacetic acid, and its silver salt (Harding and Haworth), T., 493.

$C_7H_{10}O_3$ *cyclo*Hexanone-2-carboxylic acid (Gardner, Perkin and Watson), T., 1764 ; P., 137.

$C_7H_{12}O_3$ *cyclo*Pentan-1-olacetic acid ($+ \frac{1}{2}H_2O$), and its silver salt (Harding and Haworth), T., 492.

$C_7H_{12}O_4$ Ethyl malonate, action of aromatic amines on (Chattaway and Olmsted), T., 938 ; P., 69.

$C_7H_{12}O_5$ Methyl *l*-methoxysuccinate (Purdie and Neave), T., 1517; P., 198; action of Grignard reagents on (Purdie and Arup), T., 1537 ; P., 199.

$C_7H_{12}O_6$ Methyl hydrogen *d*-dimethoxysuccinate (Purdie and Young), T., 1533.

7 III

$C_7H_4O_6N_4$ 2:5- and 2:6-Dinitro-1-methoxy-3:4-quinonediazide (Meldola and Reverdin), T., 1206.

$C_7H_5O_4N$ 5-Nitrosalicylaldehyde, and its sodium salt (Clayton), T., 1406.

$C_7H_6ON_4$ *p*-Triazobenz-*anti*- and *syn*-aldoxime (Forster and Judd), T., 257 ; P., 28.

$C_7H_6O_7N_4$ 2:3:5-Trinitro-*p*-anisidine (Meldola and Kuntzen), T., 456; P., 58; (Meldola and Reverdin), T., 1204 ; P., 132.

2:3:6-Trinitro-*p*-anisidine, product of diazotisation of (Meldola and Reverdin), T., 1204 ; P., 132.

$C_7H_8ON_2$ Phenylcarbamide, action of chlorine on (Chattaway and Chaney), T., 292 ; P., 22.

$C_7H_9O_2N$ Ethyl 1-cyano*cyclo*propane-1-carboxylate (Mitchell and Thorpe), T., 1002.

$C_7H_{10}O_2Br_2$ Allyl αβ-dibromobutyrate (James), T., 1572.

$C_7H_{10}O_3Cl_2$ αβ-Dichloroacetoacetin (Alpern and Weizmann), P., 345.

$C_7H_{10}O_4N_6$ Ethyl bistriazomalonate (Forster and Muller), T., 136 ; P., 4.

$C_7H_{11}O_2Br$ 1-Bromo*cyclo*pentaneacetic acid (Harding and Haworth), T., 492.

$C_7H_{11}O_3N$ 4-Oximino*cyclo*hexanecarboxylic acid, optically active, silver and sodium salts of (Mills and Bain), T., 1866 ; P., 214.

Ethylcarbonato*iso*butyronitrile (Davis), T., 951 ; P., 90.

$C_7H_{11}O_3N_3$ Ethyl *α*-triazomethylacetoacetate, (Forster and Newman), T., 1364; P., 197.

$C_7H_{13}O_2N$ Ethyl N-allylglycine (Alpern and Weizmann), P., 345.

$C_7H_{13}O_3N_3$ Semicarbazone of homolævulic acid (Campbell and Thorpe), T., 1315.

$C_7H_{13}NS$ Thioacetylpiperidine (Russell), T., 954.

$C_7H_{14}ON_2$ Acetenylpiperidyloxime (Russell), T., 955.

7 IV

$C_7H_2ON_2Cl_6$ 2:4:6-Trichlorophenyltrichlorocarbamide (Chattaway and Chaney), T., 299.

$C_7H_3ON_2Cl_5$ 2:4:6-Trichlorophenyldichlorocarbamide (Chattaway and Chaney), T., 298.

$C_7H_4ON_2Cl_4$ *p*-Chlorophenyltrichlorocarbamide (Chattaway and Chaney), T., 295.

2:4-Dichlorophenyl-*s*-dichlorocarbamide (Chattaway and Chaney), T., 297.

2:4-Dichlorophenyl-*as*-dichlorocarbamide (Chattaway and Chaney), T., 296.

2:4:6-Trichlorophenylmonochlorocarbamide (Chattaway and Chaney), T., 297.

$C_7H_5ON_2Cl_3$ *p*-Chlorophenyldichlorocarbamide (Chattaway and Chaney), T., 295.

2:4-Dichlorophenylmonochlorocarbamide (Chattaway and Chaney), T., 295.

2:4:6-Trichlorophenylcarbamide (Chattaway and Chaney), T., 298.

$C_7H_5O_3I_3S$ Methyl 2:3:5-, 2:4:5-, and 3:4:5-tri-iodobenzenesulphonate (Boyle), T., 218; P., 4.

$C_7H_6ON_2Cl_2$ *p*-Chlorophenylchlorocarbamide (Chattaway and Chaney), T., 294.

$C_7H_6O_3I_2S$ Methyl 2:4-, 2:5-, 3:4-, and 3:5-di-iodobenzenesulphonate (Boyle), T., 216, 220; P., 4.

$C_7H_7O_2N_3S$ Methanesulphonyl-*p*-phenylenediazoimide (Morgan, Pickard, and Micklethwait), T., 62.

$C_7H_8O_4N_2S$ Methanesulphonyl-*p*-nitroaniline (Morgan, Pickard, and Micklethwait), T., 61.

$C_7H_{10}O_2N_2S$ Methanesulphonyl-*p*-phenylenediamine and its hydrochloride (Morgan, Pickard, and Micklethwait), T., 61.

C_8 Group.

$C_8H_4O_3$ Phthalic anhydride, rate of hydration of (Rivett and Sidgwick), T., 1677; P., 200.

$C_8H_8O_2$ Anisaldehyde, condensation of, with resorcinol (Pope and Howard), T., 972; P., 88.

$C_8H_8O_3$ 4-Methoxy-2:5-toluquinone (Luff, Perkin, and Robinson), T., 1137; P., 132.

$C_8H_{10}O_3$ 4-Methoxy-2:5-toluquinol (Luff, Perkin, and Robinson), T., 1137.

$C_8H_{11}N$ Ethylaniline, absorption spectrum of (Purvis), T., 1551.

Dimethylaniline, absorption spectrum of (Purvis), T., 1551.

o-3-, and *m*-2-Xylidine, absorption spectra of (Purvis), T., 1552.

2:4:6-Trimethylpyridine, absorption spectrum of the vapour of (Purvis), T., 704.

$C_8H_{12}O_2$ *d*-1-Methyl-Δ^1-*cyclo*hexene-3-carboxylic acid (Perkin), P., 97.

dl-, *d*-, and *l*-1-Methyl-Δ^5-*cyclo*hexene-3-carboxylic acids, and calcium salt of the first (Perkin), T., 2138, 2140, 2142.

$C_8H_{12}O_3$ 1-Methyl*cyclo*hexan-2-one-3-carboxylic acid (Gardner, Perkin, and Watson), T., 1765 ; P., 137.

dl-, and *d*-1-Methyl*cyclo*hexan-3-one-4-carboxylic acids (Gardner, Perkin, and Watson), T., 1767 ; P., 137.

1-Methyl*cyclo*hexan-4-one-3-carboxylic acid (Gardner, Perkin, and Watson), T., 1769 ; P., 137.

$C_8H_{12}O_6$ Pentane-$\alpha\beta\delta$-tricarboxylic acid (Hope and Perkin), P., 178.

*iso*Pentane-$\alpha\beta\delta$-tricarboxylic acid (Hope and Perkin), P., 179.

$C_8H_{14}O_3$ 1-Methyl*cyclo*hexan-2-ol-3-carboxylic acid (Gardner, Perkin, and Watson), T., 1766.

dl-, and *d*-1-Methyl*cyclo*hexan-3-ol-4-carboxylic acids (Gardner, Perkin, and Watson), T., 1767.

1-Methyl*cyclo*hexan-4-ol-3-carboxylic acid (Gardner, Perkin, and Watson), T., 1770 ; P., 137.

$C_8H_{14}O_4$ Acid, from oxidation of carpaine (Barger), T., 471.

$C_8H_{17}N$ Coniine, absorption spectra of (Purvis), T., 1035 ; P., 113.

8 III

$C_8H_4O_4Cl_2$ 3:5-Dichloro-*o*-phthalic acid, synthesis of (Crossley and Wren), T., 98 ; P., 8.

$C_8H_6O_6N_6$ 2:5-Dinitro-4-acetylamino-3-triazophenol (Meldola and Kuntzen), P., 340.

$C_8H_6O_8N_4$ 2:3:5-Trinitro-4-acetyl-aminophenol, metallic salts of, and absorption spectrum of (Meldola and Kuntzen), T., 444 ; P., 58.

$C_8H_7ON_3$ Triazoacetophenone, and its derivatives (Forster and Müller), T., 140.

$C_8H_7O_2N_3$ Phenyltriazoacetic acid (Forster and Müller), T., 138 ; P., 4.

$C_8H_7O_2Cl$ ω-Chloro-*o*-hydroxyacetophenone (Tutin), T., 2504.

$C_8H_7O_4N$ 3-Nitro-7-methylsalicylaldehyde (Clayton), T., 1405.

5-Nitro-4-methylsalicylaldehyde (Clayton), T., 1406.

$C_8H_7O_4N_3$ ω-Triazogallacetophenone (Barger and Ewins), T., 2260.

$C_8H_7O_5N$ 5-Nitro-4-methylsalicylic acid (Clayton), T. 1402.

$C_8H_8ON_2$ Phenyliminoacetamide (Forster and Müller), T., 140.

$C_8H_8ON_4$ Triazoacetophenoneoxime (Forster and Müller), T., 141.

$C_8H_8O_4N_2$ Oxime of 5-nitro-4-methylsalicylaldehyde (Clayton), T., 1406.

$C_8H_9ON_5$ Phenyltriazomethylcarbamide (Forster and Müller), T., 1065 ; P., 113.

$C_8H_9O_2N$ ω-Amino-*p*-hydroxyacetophenone, hydriodide of (Tutin), T., 2520.

α-Cyano-Δ^1-*cyclo*penteneacetic acid (Harding and Haworth), T., 489 ; P., 61.

$C_8H_9O_3N$ ω-Amino-*op*-dihydroxyacetophenone, and its salts, (Tutin), T., 2513 ; P., 245.

ω-Amino-*mp*-dihydroxyacetophenone, hydriodide of (Tutin), T., 2520 ; P., 244.

$C_8H_9O_4N$ 5-Nitro-2-ethoxybenzaldehyde (Clayton), T., 2109.

ω-Aminogallacetophenone, hydrochloride of (Barger and Ewins), T., 2261 ; P., 248.

$C_8H_{10}O_2N_2$ Substance, from phenyltriazomethylcarbamide and sodium carbonate (Forster and Müller), T., 1065.

$C_8H_{10}O_3N$ 2:3:4-Trihydroxy-β-phenylethylamine, hydrochloride of (Barger and Ewins), T., 2260 ; P., 248.

$C_8H_{11}OCl$ 5-Chloro-1:1-dimethyl-Δ^4-*cyclo*hexen-3-one, interaction of ethyl cyanoacetate and (Crossley and Gilling), T., 518 ; P., 53.

$C_8H_{11}O_2N$ Ethyl 1-cyano*cyclo*butane-1-carboxylate, preparation of pure (Campbell and Thorpe), T., 2421.

3:4-Dihydroxy-β-phenylethylamine, preparation of, and its hydrobromide (Barger and Ewins), T., 2257 ; P., 248.

$C_8H_{12}O_2N_2$ Ethyl β-imino-α-cyanovalerate (Campbell and Thorpe), T., 1308.

$C_8H_{12}O_2Br_2$ 3:4-Dibromo-1-methyl*cyclo*hexane-3-carboxylic acid (Luff and Perkin), T., 2152.

$C_8H_{13}O_2N_3$ 4-Amino-2:4-dimethyl-Δ^2-tetrahydro-6-pyridone-3-carboxylamide, and its silver and barium salts (Chick and Wilsmore), T., 1993 ; P., 217.

$C_8H_{13}O_2Br$ 4-Bromo-1-methyl*cyclo*hexane-3-carboxylic acid (Luff and Perkin), T., 2153.

$C_8H_{13}O_3N_3$ Ethyl α-triazoethylacetoacetate (Forster and Newman), T., 1365 ; P., 197.

$C_8H_{13}O_4N_3$ Ethyl methyltriazomalonate (Forster and Müller), T., 132 ; P., 4.

$C_8H_{14}O_3N_6$ Semicarbazone of ethyl α-triazomethylacetoacetate (Forster and Newman), T., 1365.

8 IV

$C_8H_5ON_4K$ Substance, from *p*-triazobenzaldehyde and potassium cyanide (Forster and Judd), T., 260.

$C_8H_7O_3I_3S$ Ethyl 2:3:5-, 2:4:5-, and 3:4:5-tri-iodobenzenesulphonate (Boyle), T., 217 ; P., 4.

$C_8H_8O_3I_2S$ Ethyl 2:4-, 2:5-, 3:4-, and 3:5-di-iodobenzenesulphonate (Boyle), T., 216, 220 ; P., 4.

C_9 Group.

C_9H_{16} *cyclo*Geraniolene, synthesis of (Crossley and Gilling), T., 2218 ; P., 252.

9 II

$C_9H_6O_4$ Triketohydrindene hydrate (Ruhemann), T., 1446, 2025 ; P., 196, 235.

C_9H_7N Quinoline, absorption spectra of (Purvis), T., 1035 ; P., 113 ; *p*-hydroxyazo-derivatives of (Fox), T., 1337 ; P., 177.

C_9H_8O α-Hydrindone, preparation of (Mitchell and Thorpe), T., 2274.

$C_9H_8O_3$ Coumarinic acid, constitution of (Clayton), T., 2102 ; P., 230.

$C_9H_8N_2$ 3-Aminoquinoline, and its salts (Mills and Watson), T., 746 ; P., 56.

$C_9H_8Cl_4$ αβγγ-Tetrachloro-α-phenylpropane (Clarke), T., 898 ; P., 96.

C_9H_9Br Cinnamyl bromide (Clarke), T., 428.

$C_9H_{10}O_2$ 4:5- and 5:6- Dimethylsalicylaldehyde (Clayton), T., 1404.

$C_9H_{10}O_3$ α-Hydroxy-α-phenylpropionic acid, optically active, the interconversion of, and its silver salt (McKenzie and Clough), T., 1016 ; P., 85 ; conversion of, into α-chloro-α-phenylpropionic acid (McKenzie and Clough), T., 2564 ; P., 325.

α-Hydroxy-β-phenylpropionic acids, optically active, interconversion of (McKenzie and Wren), T., 1355 ; P., 181.

d- and *l*-β-Hydroxy-β-phenylpropionic acid (McKenzie and Humphries), T., 123.

5:6-Dimethylsalicylic acid (Clayton), T., 1405.

Methyl *l*-mandelate, optically active glycols from (McKenzie and Wren), T., 473 ; P., 54.

$C_9H_{10}N_2$ *p*-Amino-*m*-tolylacetonitrile, and its hydrochloride and oxalate (BARGER and EWINS), T., 2256.

$C_9H_{11}N$ *m*-Xylidine, and its condensation product with acetaldehyde, absorption spectra of (PURVIS), T., 644 ; P., 56.

$C_9H_{13}N$ Mesidine, absorption spectrum of (PURVIS), T., 1552.

1-Methyl-Δ^2-*cyclo*hexene-3-acetonitrile (HARDING and HAWORTH), T., 495.

$C_9H_{14}O_2$ 1-Methyl-Δ^2-*cyclo*hexene-3-acetic acid (HARDING and HAWORTH), T., 495.

Ethyl Δ^1-*cyclo*penteneacetate (HARDING and HAWORTH), T., 493.

$C_9H_{14}O_4$ Acid, from the sodio-derivative of dimethyl α-thujadicarboxylate, and its silver salt (THOMSON), T., 1515 ; P., 178.

$C_9H_{16}O_2$ Δ^α-Nonenoic acid, and its derivatives (HARDING and WEIZMANN), T., 299 ; P., 24.

$C_9H_{16}O_5$ Ethyl *l*-methoxysuccinate (PURDIE and NEAVE), T., 1518.

αα-Dipropionin (ALPERN and WEIZMANN), P., 345.

$C_9H_{16}O_6$ α- and β-Fructosemonoacetone (IRVINE and GARRETT), T., 1283 ; P., 143.

$C_9H_{17}Br$ 3-Bromo-1:1:3-trimethyl*cyclo*hexane (CROSSLEY and GILLING), T., 2220.

$C_9H_{18}O$ 1:1:3-Trimethyl*cyclo*hexan-3-ol (CROSSLEY and GILLING), T., 2220 ; P., 252.

$C_9H_{18}O_2$ *n*-Nonoic acid, condensation products of, with glycine, alanine and leucine (HOPWOOD and WEIZMANN), P., 69.

$C_9H_{18}O_3$ β-Hydroxy-*n*-nonoic acid (HARDING and WEIZMANN), T., 303.

9 III

$C_9H_4O_6N_2$ 3:6- and 6:8-Dinitrocoumarin (CLAYTON), T., 1397.

$C_9H_4O_7N_2$ 6:8-Dinitroumbelliferone (CLAYTON), T., 1401.

$C_9H_5O_5N$ 8-Nitroumbelliferone (CLAYTON), T., 1401.

$C_9H_6OCl_4$ ααβ-Trichloro-β-phenylpropionyl chloride (CLARKE), T., 893 ; P., 96.

$C_9H_6O_7N_2$ 6:8-Dinitrocoumarinic acid (CLAYTON), T., 1407.

C_9H_7ON 3-Hydroxyquinoline, and its sulphate (MILLS and WATSON), T., 753 ; P., 56.

8-Hydroxyquinoline, metallic salts of (FOX), T., 1119 ; P., 134.

$C_9H_7OCl_3$ αβ-Dichloro-β-phenylpropionyl chloride (CLARKE) T., 892 ; P., 96.

$C_9H_7O_2N$ 8-Aminocoumarin (CLAYTON), T., 1352.

$C_9H_7O_2Cl_3$ ααβ-Trichloro-β-phenylpropionic acid (CLARKE), T., 894 ; P., 96.

$C_9H_7O_4N_3$ Phenyltriazomalonic acid (FORSTER and MÜLLER), T., 134 ; P., 4.

$C_9H_7O_4Cl$ α-Chloro-3:4-dihydroxycinnamic acid (CLARKE), T., 897 ; P., 96.

$C_9H_7O_5N$ 5-Nitrocoumarinic acid, silver salt (CLAYTON), T., 2106.

$C_9H_7O_6N$ 8-Nitro-7-hydroxycoumarinic acid (CLAYTON), T., 1408.

$C_9H_7N_2Cl$ 2-Chloro-3-aminoquinoline (MILLS and WATSON), T., 754 ; P., 56.

$C_9H_8OCl_2$ *dl*-α-Chloro-α-phenylpropionyl chloride (MCKENZIE and CLOUGH), T., 1021.

$C_9H_8O_2N_2$ *p*-Nitro-*m*-tolylacetonitrile (BARGER and EWINS), T., 2256.

$C_9H_8O_6N_2$ 3:6-Dinitro-4:5-dimethylsalicylaldehyde (CLAYTON), T., 1407.

$C_9H_8O_7N_2$ 3:6-Dinitro-4:5-dimethylsalicylic acid (+ $\frac{1}{2}H_2O$) (CLAYTON), T., 1402.

$C_9H_8O_9N_4$ 2:3:5-Trinitro-4-acetylaminoanisole (MELDOLA and KUNTZEN), T., 455 ; P., 58.

C_9H_9ON *p*-Hydroxy-*m*-tolylacetonitrile (BARGER and EWINS), T., 2256.

$C_9H_9O_2N$ *syn*-Ethylidenesalicylamide (Hicks), T., 1034 ; P., 92.
2-Methyl-1:3-dihydrobenzoxazine-4-one (Hicks), T., 1032 ; P., 91.

$C_9H_9O_2N_5$ Phenyltriazomalonamide (Forster and Müller), T., 136 ; P., 4.

$C_9H_9O_2Cl$ *d*- and *l*-*α*-Chloro-*α*-phenylpropionic acid (McKenzie and Clough), T., 1021.
ω-Chloro-*o*-methoxyacetophenone (Tutin), T., 2503 ; P., 244.

$C_9H_9O_2Br$ Benzyl bromoacetate (Clarke), T., 428.

$C_9H_9O_3N$ Malonanilic acid, preparation of (Chattaway and Olmsted), T., 939.

$C_9H_9O_4N$ 3-Nitro-4:5- and 5:6-dimethylsalicylaldehyde (Clayton), T., 1405.

$C_9H_{10}ON_6$ Triazoacetophenonesemicarbazone (Forster and Müller), T., 141.

$C_9H_{11}O_2N$ Methyl *α*-cyano-Δ^1-*cyclo*penteneacetate (Harding and Haworth), T., 490.
ω-Amino-*p*-methoxyacetophenone, salts of (Tutin), T., 2509.

$C_9H_{11}O_4N_3$ 2:5-Dinitrodimethyl-*p*-toluidine (Morgan and Clayton), T., 2650 ; P., 323.
2:6-Dinitrodimethyl-*p*-toluidine (Morgan and Clayton), T., 2652 ; P., 323.

$C_9H_{11}O_5N_3$ 2:6-Dinitrodimethyl-*p*-anisidine (Meldola), P., 232.

$C_9H_{11}O_8N_7$ Guanidine salt of 2:3:5-trinitro-4-acetylaminophenol (Meldola and Kuntzen), T., 452.

$C_9H_{11}NS$ *N*-Methylthiodiphenylamine, mercuri-iodide of (Barnett and Smiles), T., 985.

$C_9H_{13}ON$ *p*-Hydroxyphenylethylmethylamine, and its hydrochloride picrate, oxalate and picronolate (Walpole), T., 945 ; P., 88.
4-Hydroxy-*β*-*m*-tolylethylamine, and its salts (Barger and Ewins), T., 2257 ; P., 248.

$C_9H_{13}O_2N$ *β*-Amino-*β′*-phenoxy*iso*propyl alcohol, and its salts (Boyd), T., 1791 ; P., 209.
3:4-Dihydroxyphenylethylmethylamine, and its salts (Pyman), T., 272.
4:5-Dimethoxy-*o*-toluidine (Luff, Perkin, and Robinson), T., 1134 ; P., 132.

$C_9H_{13}O_3N$ Ethyl cyano*iso*butyrylacetate, and its silver salt (Campbell and Thorpe), T., 1311.

$C_9H_{14}O_2N_2$ Ethyl *β*-imino-*α*-cyano*iso*butylacetate (Campbell and Thorpe), T., 1311.

$C_9H_{15}OCl$ Δ^{α}-Nonenoyl chloride (Harding and Weizmann), T., 302.

$C_9H_{15}O_2Br$ Ethyl 1-bromo*cyclo*pentaneacetate (Harding and Haworth), T., 493.

$C_9H_{15}O_3N$ Amide of *α*-thujadicarboxylic acid, and its ammonium salt (Thomson), T., 1512.

$C_9H_{15}O_4N_3$ Ethyl ethyltriazomalonate (Forster and Müller), T., 133 ; P., 4.

$C_9H_{16}O_2Br_2$ *αβ*-Dibromo-*n*-nonoic acid (Harding and Weizmann), T., 304.

$C_9H_{16}O_3N_6$ Semicarbazone of ethyl *α*-triazoethylacetoacetate (Forster and Newman), T., 1366.

$C_9H_{17}ON$ Δ^{α}-Nonenoamide (Harding and Weizmann), T., 302.

9 IV

$C_9H_6O_3NCl_3$ 2:4:6-Trichloromalonanilic acid (Chattaway and Mason), T., 343.

$C_9H_6O_3NBr_3$ 2:4:6-Tribromomalonanilic acid (Chattaway and Mason), T., 345.

$C_9H_7O_3NCl_2$ 2:4-Dichloromalonanilic acid (Chattaway and Mason), T., 342.

$C_9H_7O_3NBr_2$ 2:4-Dibromomalonanilic acid (Chattaway and Mason), T., 344.

$C_9H_8O_3NCl$ *p*-Chloromalonilic acid (Chattaway and Mason), T., 341.

$C_9H_8O_3NBr$ *p*-Bromomalonanilic acid (Chattaway and Mason), T., 344.

$C_9H_{16}OClBr$ *a*-Bromo-*n*-nonoyl chloride (Hopwood and Weizmann), P., 69.

C_{10} Group.

$C_{10}H_8$ Naphthalene, absorption spectrum of (Homer and Purvis), T., 280; P., 5; the Friedel-Crafts' reaction applied to (Homer), T., 1141; P., 11.

$C_{10}H_{10}$ 1:4-Dihydronaphthalene, absorption spectrum of (Leonard), T., 1246; P., 143.

$C_{10}H_{12}$ 1:2:3:4-Tetrahydronaphthalene, absorption spectrum of (Leonard), T., 1246; P., 143.

$C_{10}H_{16}$ Terpene, monocyclic, from thymol (Henderson and Sutherland), T., 1619; P., 203.

$\Delta^{3:8(9)}$-*p*-Menthadiene, new method of preparation of (Perkin and Wallach), T., 1427; P., 194.

dl-$\Delta^{4:8(9)}$-*m*-Menthadiene (Perkin), T., 2147.

dl-, *d*-, and *l*-$\Delta^{5:8(9)}$-*m*-Menthadiene (Perkin), T., 2139, 2142.

d-Carvestrene (*sylvestrene*), synthesis of, and its dihydrochloride (Perkin), P., 97.

$C_{10}H_{18}$ 1:1-Dimethyl-3-ethyl*cyclo*hexene (Crossley and Gilling), T., 2222.

Dihydrocamphene, preparation of (Henderson and Pollock), T., 1621; P., 203.

Dihydrobornylene, preparation of (Henderson and Pollock), T., 1621; P., 204.

10 II

$C_{10}H_6O_8$ Mellophanic acid (*benzene*-1:2:3:4-*tetracarboxylic acid*), constitution of (Bamford and Simonsen), T., 1908; P., 206.

Prehnitic acid (*benzene*-1:2:3:5-*tetracarboxylic acid*), constitution of (Bamford and Simonsen), T., 1906; P., 206.

$C_{10}H_6N_6$ 2:7-Bistriazonaphthalene (*naphthylene*-2:7-*bisazoimide*) (Morgan and Micklethwait), T., 2560; P., 293.

$C_{10}H_7N_3$ 1:2-Naphthylenediazoimine, two isomerides (Morgan and Godden), T., 1718.

$C_{10}H_8O_6$ Methyltrimesic acid, and its silver salt (Simonsen), T., 1914; P., 200.

$C_{10}H_8N_2$ 1-Imino-2-cyanohydrindene (Mitchell and Thorpe), T., 2276.

$C_{10}H_9O_3$ *d*-*β*-Phenyl-*β*-methylglycidic acid, sodium salt (Wootton), T., 409; P., 44.

$C_{10}H_{10}O$ 2-Methyl-1-hydrindone (Mitchell and Thorpe), T., 2275.

$C_{10}H_{10}O_6$ *m*-Hemipinic acid, preparation of (Luff, Perkin, and Robinson), T., 1136; P., 132.

$C_{10}H_{12}O_2$ 3:5-Diethyl-*p*-benzoquinone (Henderson and Boyd), T., 1664.

$C_{10}H_{12}O_3$ Methyl *l*-phenylmethoxyacetate (McKenzie and Wren), T., 484.

$C_{10}H_{12}O_4$ *β*-5-Hydroxy-3-methoxyphenylpropionic acid (Salway), T., 2417.

2:3:4-Trimethoxybenzaldehyde (Barger and Ewins), T., 2258.

$C_{10}H_{12}O_5$ Asaronic acid, preparation of (Luff, Perkin, and Robinson), T., 1138; P., 133.

$C_{10}H_{12}N_2$ 3-*β*-Aminoethylindole, syntheses of (Ewins and Laidlaw), P., 343.

$C_{10}H_{13}N$ 2-Methyltetrahydroquinoline (*tetrahydroquinaldine*), racemic, resolution of (Pope and Read) T., 2199; P., 251.

d- and *l*-2-Methyltetrahydroquinoline, and their hydrochlorides (Pope and Read), T., 2203.

$C_{10}H_{14}O$ Methylpropylphenol (Henderson and Boyd), T., 1669.

$C_{10}H_{14}O_2$ *l*-*αβ*-Dihydroxy-*α*-phenyl*iso*butane (McKenzie and Wren), T., 481.
 3:5-Diethylquinol (Henderson and Boyd), T., 1665.

$C_{10}H_{14}O_3$ 2:4:5-Trimethoxytoluene (Luff, Perkin, and Robinson), T., 1137; P., 133.

$C_{10}H_{14}O_4$ Tetrahydroxy*tert.*-butylbenzene (Henderson and Boyd), T., 1665.
 Tetrahydroxycymene (Henderson and Boyd), T., 1663.

$C_{10}H_{14}N_2$ Nicotine, absorption spectra of (Purvis), T., 1035; P., 113.

$C_{10}H_{15}N$ Diethylaniline, absorption spectrum of (Purvis), T., 1551.
 α-1-Methyl-Δ^2-*cyclo*hexene-3-propionitrile (Harding and Haworth), T., 496.

$C_{10}H_{16}O$ Camphor, vapour pressure of (Vanstone), T., 429; P., 47; absorption spectra of the acyl-derivatives of (Lowry and Southgate), T., 905; P., 68; freezing-point curve for mixtures of, and phenol (Wood and Scott), T., 1573; P., 194; mercury compounds of, action of halogens on (Marsh), T., 2410; P., 297.
 Tanacetone (*β-thujone*), and its derivatives (Thomson), T., 1502; P, 177.

$C_{10}H_{16}O_2$ *α*-1-Methyl-Δ^2-*cyclo*hexene-3-propionic acid (Harding and Haworth), T., 497.
 Ethyl *d*-1-methyl-Δ^1-*cyclo*hexene-3-carboxylate (Perkin), P., 97.
 Ethyl 1-methyl-Δ^4-*cyclo*hexene-3-carboxylate (Perkin), T., 2146.
 Ethyl *dl*-, *d*-, and *l*-1-methyl-Δ^5-*cyclo*hexene-3-carboxylate (Perkin), T., 2139, 2140, 2143.

$C_{10}H_{16}O_3$ Ethyl *dl*- and *d*-methyl*cyclo*hexan-3-one-4-carboxylates (Gardner, Perkin, and Watson), T., 1767.

$C_{10}H_{16}O_4$ Camphoric acid, Komppa's synthesis of (Blanc and Thorpe), T., 836; P., 83; synthesis of (Komppa), P., 328; mono-aryl esters of (Edminson and Hilditch), T., 224; action of the Grignard reagent on esters of (Shibata), T., 1239; P., 141.
 *iso*Camphoric acid, action of the Grignard reagent on esters of (Shibata), T., 1239; P., 141.
 Lactone of *α*-methyl-*γ*-hydroxy*iso*propyladipic acid, *cis*- and *trans*- (Perkin), T., 2144.

$C_{10}H_{18}O$ Borneol, vapour pressure of (Vanstone), T., 429; P., 47.
 Δ^3-*p*-Menthenol(8), new method of preparation of (Perkin and Wallach), T., 1427; P., 194.
 dl-Δ^4-*m*-Menthenol(8) (Perkin), T., 2147.
 dl-, *d*-, and *l*-Δ^5-*m*-Menthenol(8) (Perkin), T., 2139, 2141, 2143.
 d-Dihydrocarvestrenol (Perkin), P., 97.

$C_{10}H_{18}O_3$ Ethyl 1-methyl*cyclo*hexan-4-ol-3-carboxylate (Gardner, Perkin, and Watson), T., 1770.

$C_{10}H_{19}Br$ 3-Bromo-1:1-dimethyl-3-ethyl*cyclo*hexane (Crossley and Gilling), T., 2222.

$C_{10}H_{20}O$ 1:1-Dimethyl-3-ethyl*cyclo*hexan-3-ol (Crossley and Gilling), T., 2222.

$C_{10}H_{20}O_2$ Menthane-2:5-diol (Henderson and Sutherland), T., 1618; P., 203.

$C_{10}H_{20}O_4$ *γδ*-Dimethoxy-*βε*-dimethylhexane-*βε*-diol (Purdie and Young), T., 1534; P., 198.

10 III

$C_{10}H_5O_3N$ Substance, from triketohydrindene and hydrogen cyanide (Ruhemann), T. 2029; P., 235.

$C_{10}H_5O_3Cl_5$ *αβ*-Dichloro-3:4-dichloromethylenedioxy-*β*-phenylpropiony chloride (Clarke), T., 896; P., 96.

$C_{10}H_5O_5Cl$ α-Chloro-3:4-carbonyldioxycinnamic acid (CLARKE), T., 897; P., 96.

$C_{10}H_6O_4Br_2$ Dibromoscopoletin (MOORE), T., 2229.

$C_{10}H_6O_5Cl_2$ αβ-Dichloro-3:4-carbonyldioxy-β-phenylpropionic acid (CLARKE), T., 896; P., 96.

$C_{10}H_6O_6N_2$ 3:6-Dinitro-7-methylcoumarin (CLAYTON), T., 1398.

$C_{10}H_6N_3Br$ 4-Bromonaphthylene-1-diazo-2-imine (MORGAN and GODDEN), T., 1712.

$C_{10}H_7ON$ 2-Cyano-1-hydrindone (MITCHELL and THORPE), T., 2277.

$C_{10}H_7O_4N$ 6-Nitro-7-methylcoumarin (CLAYTON), T., 1397.
 8-Nitro-7-methylcoumarin (CLAYTON), T., 1406.

$C_{10}H_8ON_2$ Quinoline-3-carboxyamide (MILLS and WATSON), T., 745; P., 56.

$C_{10}H_8NI$ 4-Iodo-α-naphthylamine (MORGAN and GODDEN), T., 1717.

$C_{10}H_9O_2N$ Benzoyl-lactonitrile (DAVIS), T., 950; P., 89.
 6-Amino-7-methylcoumarin (CLAYTON), T., 1352.

$C_{10}H_9O_2Cl_3$ Methyl ααβ-trichloro-β-phenylpropionate (CLARKE), T., 895; P., 96.

$C_{10}H_9O_3N_3$ Substance, from guanidine and triketohydrindene (RUHEMANN), T., 2028; P., 235.

$C_{10}H_9O_5N$ Methyl ether of 5-nitrocoumaric acid, silver salt of (CLAYTON), T., 2108.
 Methyl ether of 5-nitrocoumarinic acid, and silver salt (CLAYTON), T., 2107.

$C_{10}H_9N_2Br$ 4-Bromo-1:2-naphthylenediamine (MORGAN and GODDEN), T., 1710.

$C_{10}H_{10}O_5N_2$ ω-5-Dinitro-2-hydroxy-α-4-dimethylstyrene, and its sodium salt (CLAYTON), T., 1407.

$C_{10}H_{11}O_2N$ 4:5-Dimethoxy-*o*-toluonitrile (LUFF, PERKIN, and ROBINSON), T., 1135; P., 132.
 Phenolbetaine of 6:7-dihydroxy-2-methyl-3:4-dihydro*iso*quinolinium hydroxide (and + H_2O and $1\frac{1}{2}H_2O$) (PYMAN), T., 276.

$C_{10}H_{11}O_2N_3$ Ethyl phenyltriazoacetate (FORSTER and MÜLLER), T., 138; P., 4.

$C_{10}H_{11}O_3N$ Malono-*o*- and *p*-toluidic acid, preparation of (CHATTAWAY and OLMSTED), T., 940.
 6:7-Dihydroxy-1-keto-2-methyltetrahydro*iso*quinoline (PYMAN), T., 271.

$C_{10}H_{11}O_3Cl$ ω-Chloro-*op*-dimethoxyacetophenone (TUTIN), T., 2512; P., 244.
 ω-Chloro-*mp*-dimethoxyacetophenone (TUTIN), T., 2510; P., 244.

$C_{10}H_{12}N_6Fe$ Tetramethyl ferrocyanide, derivatives of (HARTLEY), T., 1066, 1725; P., 90, 210.

$C_{10}H_{13}O_2N$ α-Cyano-1-methyl-Δ^2-*cyclo*hexene-3-acetic acid (HARDING and HAWORTH), T., 494.
 Ethyl α-cyano-Δ^1-*cyclo*penteneacetate (HARDING and HAWORTH), T., 489; P., 61.
 Methyl α-cyano-α-Δ^1-*cyclo*pentenepropionate (HARDING and HAWORTH), T., 490.
 3:5-Diethyl-*p*-benzoquinone oxime (HENDERSON and BOYD), T., 1664.
 6:7-Dihydroxy-2-methyltetrahydro*iso*quinoline, and its hydrochloride and picrate (PYMAN), T., 275.

$C_{10}H_{13}O_2Cl$ γ-Chloro-β-hydroxy-α-*o*- and *p*-tolyloxypropane (BOYD and MARLE), T., 1790; P., 208.

$C_{10}H_{13}O_3N$ β-3-Methoxy-4:5-methylenedioxyphenylethylamine, and its hydrochloride (SALWAY), T., 1212.
 Ethyl α-cyano-β-*cyclo*butylformylacetate (CAMPBELL and THORPE), T., 2424.

$C_{10}H_{13}O_3N$ β-5-Hydroxy-3-methoxyphenylpropionamide (SALWAY), T., 2417.

6:7-Dihydroxy-2-methyl-3:4-dihydro*iso*quinolinium hydroxide, its chloride, picrate, and sodium salt (PYMAN), T., 276.

$C_{10}H_{14}O_2N_2$ Ethyl β-imino-α-cyano-β-*cyclo*butylpropionate (CAMPBELL and THORPE), T., 2424.

$C_{10}H_{14}O_4N_2$ Ethyl β-imino-α-cyanoglutarate, constitution of (CAMPBELL and THORPE), T., 1299; P., 176.

Ethyl hydrogen β-imino-α′-cyano-αα-dimethylglutarate (CAMPBELL and THORPE), T., 1311.

$C_{10}H_{15}ON$ *p*-Hydroxyphenylethylethylamine, and its oxalate, hydrochloride and picronolate (WALPOLE), T., 948; P., 88.

$C_{10}H_{15}O_2N$ 3:4-Dihydroxyphenylethylethylamine, and its hydrochloride (PYMAN), T., 274.

Camphorimide, *N*-alkyl and aryl derivatives of (WOOTTON), T., 415.

d-Camphorimide, preparation of, and its derivatives (EVANS), T., 2237; P., 251.

$C_{10}H_{16}ON_2$ α-, and β- Camphorquinonehydrazone (FOSTER and ZIMMERLI), T., 2165; P., 245.

$C_{10}H_{16}O_3S_2$ Camphor-β-thiosulphonic acid, and its sodium salt (HILDITCH), T., 1098; P., 96.

$C_{10}H_{16}O_4S$ Camphor-β-sulphonic acid, mono-aryl esters of (EDMINSON and HILDITCH), T., 228.

d- and *l*- Camphor-β-sulphonic acid, *d*- and *l*-pavine and metallic salts of, rotatory power of (POPE and GIBSON), T., 2211; P., 250.

d- and *l*- Camphor-π-sulphonic acid, ammonium salts of (POPE and READ), T., 990.

$C_{10}H_{17}ON$ Dimethylethyl*cyclo*hexanoneoxime (CROSSLEY and GILLING), T., 534.

$C_{10}H_{17}O_3N$ α-Camphoramic acid, alkyl and aryl derivatives of (WOOTTON), T., 413.

$C_{10}H_{19}ON$ 3-Ethoxy-1:1-dimethyl-Δ^3-*cyclo*hexenylidene-5-propionitrile (CROSSLEY and GILLING), T., 534.

10 IV

$C_{10}H_6O_7N_4Cr_2$ Naphthalene-2:7-bisdiazonium dichromate (MORGAN and MICKLETHWAIT), T., 2558; P., 293.

$C_{10}H_6N_4Cl_6Pt$ Naphthalene-2:7-bisdiazonium platinichloride (MORGAN and MICKLETHWAIT), T., 2558; P., 293.

$C_{10}H_6N_4Cl_8Au$ Naphthalene-2:7-bisdiazonium aurichloride (MORGAN and MICKLETHWAIT), T., 2558; P., 293.

$C_{10}H_7ON_2Cl$ 2-Chloroquinoline-3-carboxylamide (MILLS and WATSON), T. 754; P., 56.

$C_{10}H_8O_8N_4S_2$ Naphthalene-2:7-bisdiazonium sulphate (+½EtOH) (MORGAN and MICKLETHWAIT), T., 2558; P., 293.

$C_{10}H_{12}O_3NAg$ Silver derivative of α-cyano-β-*cyclo*butylformylacetic acid (CAMPBELL and THORPE), T., 2424.

$C_{10}H_{14}O_2NBr$ *d*-Camphorbromoimide (EVANS), T., 2238.

$C_{10}H_{14}O_2NI$ *d*-Camphoriodoimide (EVANS), T., 2239.

$C_{10}H_{14}O_2NNa$ *d*-Camphorsodioimide (EVANS), T., 2241.

$C_{10}H_{15}O_4BrS$ *d*-Bromocamphorsulphonic acid, *d*- and *l*-narcotine salts of (PERKIN and ROBINSON), P., 131.

dl- and *l*-α-Bromocamphor-π-sulphonic acid, *dl*-, and *d*-pavine salts of (POPE and GIBSON), T., 2209.

C_{11} Group.

$C_{11}H_{10}O_3$ Piperonylideneacetone, isomerides, action of light on (Stobbe and Wilson), T., 1722; P., 206.

$C_{11}H_{10}O_7$ 6-Carboxy-3:4-dimethoxyphenylglyoxylic acid, synthesis of, and distillation of its silver salt (Harding and Weizmann), T., 1129; P., 130.

$C_{11}H_{12}O_5$ 4:5-Dimethyl-*o*-tolylglyoxylic acid (Harding and Weizmann), T., 1128.

$C_{11}H_{14}O_3$ Ethyl *l*-*a*-hydroxy-*a*-phenylpropionate (McKenzie and Clough), T., 2569; P., 325.

4:5-Dimethoxy-*o*-methylacetophenone (Harding and Weizmann), T., 1128; P., 130.

$C_{11}H_{14}O_4$ *β*-3:5-Dimethoxyphenylpropionic acid (Salway), T., 2417.

$C_{11}H_{16}O_3$ Camphorcarboxylic acid, absorption spectra of, and its derivatives (Lowry, Desch, and Southgate), T., 899; P., 68.

$C_{11}H_{16}O_5$ Ethyl *a*-acetylglutaconate (Simonsen), T., 1914.

Ethyl *cyclo*pentan-1-one-2:5-dicarboxylate (Mitchell and Thorpe), T., 1003.

$C_{11}H_{16}O_7$ *aa*-Diacetoacetin (Alpern and Weizmann), P., 345.

$C_{11}H_{18}O_3$ *d*-*iso*Menthonecarboxylic acid (Gardner, Perkin, and Watson), T., 1770.

$C_{11}H_{18}O_4$ Methyl hydrogen camphorate (Edminson and Hilditch), T., 225.

Dimethyl *a*-thujadicarboxylate (Thomson), T., 1513; P., 178.

$C_{11}H_{20}O_3$ *d*-*iso*Mentholcarboxylic acid (Gardner, Perkin, and Watson), T., 1771.

$C_{11}H_{20}O_5$ Propyl *l*-methoxysuccinate (Purdie and Neave), T., 1518.

$C_{11}H_{22}O_3$ Ethyl *β*-hydroxy-*n*-nonoate (Harding and Weizmann), T., 303.

11 III

$C_{11}H_7O_9N_3$ 3:5:8-Trinitro-6:7-dimethylcoumarin (Clayton), T., 1399.

$C_{11}H_8O_6N_2$ 3:6-Dinitro-4:7-dimethylcoumarin (Clayton), T., 1398.

5:8-Dinitro-6:7-dimethylcoumarin (Clayton), T., 1399.

$C_{11}H_9ON$ 2-Cyano-3-methoxyindene (Mitchell and Thorpe), T., 2278.

$C_{11}H_9O_4N$ 6-Nitro-4:7-dimethylcoumarin (Clayton), T., 1398.

8-Nitro-5:6-dimethylcoumarin (Clayton), T., 1405.

5-Nitro-6:7-dimethylcoumarin (Clayton), T., 1398.

8-Nitro-6:7-dimethylcoumarin (Clayton), T., 1405.

$C_{11}H_{10}ON_2$ 3-Acetylaminoquinoline (Mills and Watson), T., 753; P., 56.

$C_{11}H_{10}O_3N_6$ Triketohydrindene disemicarbazone (Ruhemann), T., 1448.

$C_{11}H_{10}O_4N_2$ *m*-Nitrobenzoyl*iso*butyronitrile (Davis), T., 951.

$C_{11}H_{11}O_2N$ 6-Amino-4:7-dimethylcoumarin (Clayton), T., 1352.

5-Amino-6:7-dimethylcoumarin (Clayton), T., 1353.

Benzoyloxy*iso*butyronitrile (Davis), T., 951; P., 90.

$C_{11}H_{11}O_5N$ Methyl ether of methyl 5-nitrocoumarate (Clayton), T., 2108.

Methyl ether of methyl 5-nitrocoumarinate (Clayton), T., 2107.

Ethyl ether of 5-nitrocoumaric acid, and silver salt (Clayton), T., 2109.

Ethyl ether of 5-nitrocoumarinic acid, and silver salt (Clayton), T., 2107.

$C_{11}H_{11}O_7N$ Oxime of 6-carboxy-3:4-dimethoxyphenylglyoxylic acid (Harding and Weizmann), T., 1130.

$C_{11}H_{12}O_2N_2$ 5:8-Diamino-6:7-dimethylcoumarin (Clayton), T., 1354.

$C_{11}H_{13}ON_3$ 2-Methyl-1-hydrindone semicarbazone (Mitchell and Thorpe), T., 2275.

$C_{11}H_{13}O_2N$ Phenolbetaine of 6:7-dihydroxy-2-ethyl-3:4-dihydro*iso*quinolinium hydroxide (Pyman), T., 280.

$C_{11}H_{13}O_3N$ 7 (or 6)-Hydroxy-1-keto-6 (or 7)-methoxy-2-methyltetrahydro*iso*quinoline, and its sodium salt (Pyman), T., 271.

6:7-Dihydroxy-1-keto-2-ethyltetrahydro*iso*quinoline (Pyman), T., 274.

$C_{11}H_{13}O_4N$ β-3-Methoxy-4:5-methylenedioxyphenylpropionamide (Salway), T., 1211.

$C_{11}H_{14}O_4N_2$ Ethyl β-imino-α-cyano-1-carboxy-β-*cyclo*butyl-1-propionate, α- and β-forms of (Campbell and Thorpe), T., 2422.

$C_{11}H_{15}ON$ Cyanocarone (Clarke and Lapworth), T., 11.

Substance, from *p*-toluidine and acetaldehyde, α- and β- forms (Jones and White), T., 643 ; absorption spectra of (Purvis), T., 646.

$C_{11}H_{15}ON_3$ Camphane-oxytriazine (Foster and Zimmerli), T., 2176.

$C_{11}H_{15}O_2N$ Acetyl-*p*-hydroxyphenylethylmethylamine (Walpole), T., 943.

$C_{11}H_{15}O_3N$ Acetyl derivative of 4:5-dimethoxy-*o*-toluidine (Luff, Perkin, and Robinson), T., 1135 ; P., 132.

β-3:5-Dimethoxyphenylpropionamide (Salway), T., 2417.

6:7-Dihydroxy-2-ethyl-3:4-dihydro*iso*quinolinium hydroxide, its chloride and picrate (Pyman), T., 280.

$C_{11}H_{15}O_3N_3$ 5-Nitro-2-acetylamino-dimethyl-*p*-toluidine (Morgan and Clayton), T., 2650 ; P., 323.

$C_{11}H_{16}O_2N_2$ α-Formylcamphorquinonehydrazone (Foster and Zimmerli), T., 2168.

Pilocarpine, constitution of (Pyman), T., 1814 ; P., 211.

$C_{11}H_{17}ON_3$ 2-Acetyl-2:5-diaminodimethyl-*p*-toluidine (Morgan and Clayton), T., 2651 ; P., 323.

$C_{11}H_{17}O_2N$ 3:4-Dihydroxyphenylethylpropylamine, and its hydrochloride (Pyman), T., 275.

Camphorcarboxyamide (Glover and Lowry), P., 162.

d-Camphormethylimide, preparation of (Evans), T., 2239.

Substance, from action of sodium hydroxide on cyanocarone (Clarke and Lapworth), T., 15.

$C_{11}H_{17}O_2N_3$ Camphorquinone α- and β-semicarbazone (Forster and Zimmerli), T., 2173 ; P. 246.

$C_{11}H_{17}O_4N$ Ethyl 2-imino*cyclo*pentane-1:3-dicarboxylate (Mitchell and Thorpe), T., 1002 ; P., 114.

$C_{11}H_{18}O_3S_2$ Camphoryl methyl-β-disulphoxide (Hilditch), T., 1098 ; P., 96.

$C_{11}H_{18}O_4S$ Methyl camphor-β-sulphonate (Edminson and Hilditch), T., 226.

$C_{11}H_{20}O_4N_2$ *d*-Camphor-*p*-nitrobenzylimide (Evans), T. 2241.

$C_{11}H_{22}O_3N_2$ α-Amino-*n*-nonoylglycine (Hopwood and Weizmann), P., 70.

11 IV

$C_{11}H_{10}O_3NCl_3$ Ethyl 2:4:6-trichloromalonanilate (Chattaway and Mason), T., 343.

$C_{11}H_{10}O_3NBr_3$ Ethyl 2:4:6-tribromomalonanilate (Chattaway and Mason), T., 345.

$C_{11}H_{11}O_3NCl_2$ Ethyl 2:4-dichloromalonanilate (Chattaway and Mason), T., 342.

$C_{11}H_{11}O_3NBr_2$ Ethyl 2:4-dibromomalonanilate (Chattaway and Mason), T., 344.

$C_{11}H_{11}O_5NBr_2$ Methyl αβ-dibromo-5-nitro-2-methoxy-β-phenylpropionate (Clayton), T., 2110.

$C_{11}H_{12}O_3NCl$ Ethyl *p*-chloromalonanilate (Chattaway and Mason), T., 341.

$C_{11}H_{12}O_3NBr$ Ethyl *p*-bromomalonanilate (Chattaway and Mason), T., 344.

$C_{11}H_{14}O_2NCl$ 7 (or 6)-Hydroxy-6 (or 7)-methoxy-2-methyl-3:4-dihydro*iso*quinolinium chloride (Pyman), T., 278.

$C_{11}H_{14}O_2NI$ 7 (or 6)-Hydroxy-6 (or 7)-methoxy-2-methyl-3:4-dihydro*iso*quinolinium iodide (Pyman), T., 278.

$C_{11}H_{16}O_2NBr$ Camphorcarboxybromoamide (Glover and Lowry), P., 163.

$C_{11}H_{18}O_2NCl$ 3:4-Dihydroxy-β-phenylethyltrimethylammonium chloride (Barger and Ewins), T., 2258.

$C_{11}H_{20}O_3NBr$ α-Bromo-*n*-nonoylglycine (Hopwood and Weizmann), P., 69.

C_{12} Group.

$C_{12}H_9I$ Iodoacenaphthene, and its picrate (Crompton and Harrison), P., 226.

$C_{12}H_{12}O_3$ 5-Hydroxy-4:6:8-trimethylcoumarin (Clayton), T., 1403.

Ethyl 1-hydrindone-2-carboxylate (Mitchell and Thorpe), T., 2273; P., 249.

$C_{12}H_{14}O_4$ Hydroxydiacetyldimethoxybenzene (Tutin and Caton), T., 2065; P., 223.

$C_{12}H_{14}O_6$ Ethyl 6-methyl-2-pyrone-3:5-dicarboxylate, conversion of, into methyltrimesic acid (Simonsen), T., 1910; P., 200.

$C_{12}H_{16}O_5$ 2:3:4-Trimethoxy-β-phenylpropionic acid (Barger and Ewins), T., 2259.

$C_{12}H_{18}O_5$ *d-iso*Menthonedicarboxylic acid (Gardner, Perkin, and Watson), T., 1772.

$C_{12}H_{20}O_4$ Ethyl hydrogen camphorate (Edminson and Hilditch), T., 225.

Dimethyl-*l-iso*camphorate (Shibata), T., 1245.

$C_{12}H_{22}O_6$ Trimethylfructosemonoacetone (Irvine and Garrett), T., 1283.

$C_{12}H_{24}O_2$ Lauric acid, condensation products of, with glycine, alanine, and leucine (Hopwood and Weizmann), P., 69.

12 III

$C_{12}H_8OS_2$ Monoxide of diphenylene *p*-disulphide (Hilditch), T., 2586.

$C_{12}H_8O_2S_2$ Diphenylene *p*-disulphoxide (Hilditch), T., 2585.

$C_{12}H_8O_4S_2$ Substance, from oxidation of diphenylene *p*-disulphoxide ($+2H_2O$) (Hilditch), T., 2588.

$C_{12}H_9O_8N_3$ 3:5:8-Trinitro-4:6:7-trimethylcoumarin (Clayton), T., 1399.

3:5:7-Trinitro-4:6:8-trimethylcoumarin (Clayton), T., 1400.

$C_{12}H_9O_8N_5$ Substance, from *o*- and *m*-nitroanilines and trinitrobenzene (Sudborough and Beard), T., 783.

$C_{12}H_9N_4Cl$ Benzeneazobenzenediazonium chloride (Hewitt and Thole), T., 514; P., 54.

$C_{12}H_{10}O_5N_2$ Substance, from ethyl 1-iminohydrindene-2-carboxylate and nitrous acid (Mitchell and Thorpe), T., 2272.

$C_{12}H_{10}O_6N_2$ 5·7-Dinitro-4:6:8-trimethylcoumarin (Clayton), T., 1400.

$C_{12}H_{11}O_3K$ Potassium compound of ethyl 1-hydrindrone-2-carboxylate (Mitchell and Thorpe), T., 2273.

$C_{12}H_{11}O_4N$ 6-Nitro-3:4:7-trimethylcoumarin (Clayton), T., 1358.

8-Nitro-4:6:7-trimethylcoumarin (Clayton), T., 1399.

5-Nitro-4:6:8-trimethylcoumarin (Clayton), T., 1400.

7-Nitro-5:6:8-trimethylcoumarin (Clayton), T., 1400.

$C_{12}H_{12}O_5N_2$ 5(or 8)-Nitro-6:7-dimethoxy-2-methyl-1:2-dihydro*iso*quinoline (PYMAN), T., 270.

$C_{12}H_{13}O_2N$ 6-Amino-3:4:7-trimethylcoumarin (CLAYTON), T., 1354.

6-Amino-4:6:7-trimethylcoumarin (CLAYTON), T., 1353.

5-Amino-4:6:8-trimethylcoumarin (CLAYTON), T., 1403.

7-Amino-5:6:8-trimethylcoumarin (CLAYTON), T., 1353.

Ethyl 1-iminohydrindene-2-carboxylate (MITCHELL and THORPE), T., 2271; P., 249.

$C_{12}H_{13}O_5N$ Methyl ether of ethyl 5-nitrocoumarate (CLAYTON), T., 2108.

Ethyl ether of methyl 5-nitrocoumarate (CLAYTON), T., 2109.

Methyl ether of ethyl 5-nitrocoumarinate (CLAYTON), T., 2108.

Ethyl ether of methyl 5-nitrocoumarinate (CLAYTON), T., 2108.

$C_{12}H_{14}O_2N_2$ 5:7-Diamino-4:6:8-trimethylcoumarin (CLAYTON), T., 1354.

$C_{12}H_{15}O_3N$ 3-Methoxy-1:1-dimethyl-Δ^3-*cyclo*hexenylidene-5-cyanoacetic acid (CROSSLEY and GILLING), T., 530.

6:7-Dihydroxy-1-keto-2-propyltetrahydro*iso*quinoline (PYMAN), T., 275.

$C_{12}H_{15}O_4N$ Cotarnine, synthesis of, and its aurichloride and picrate (SALWAY), T., 1208; P., 98, 138.

*neo*Cotarnine, and its hydrochloride ($+1\frac{1}{2}H_2O$), picrate and aurichloride (SALWAY), T., 1217.

$C_{12}H_{15}NS$ Thiobenzoylpiperidine (RUSSELL), T., 955.

$C_{12}H_{16}O_2N_2$ Nitroso- derivatives of ethylidenexylidine (JONES and WHITE), T., 642.

$C_{12}H_{17}ON$ α-and β-Ethylidenexylidine (JONES and WHITE), T., 639; absorption spectra of (PURVIS), T., 647.

3-Ethoxy-1:1-dimethyl-Δ^3-*cyclo*hexenylidene-5-acetonitrile (CROSSLEY and GILLING), T., 531.

$C_{12}H_{17}O_2N$ Acetyl-*p*-methoxyphenylethylmethylamine (WALPOLE), T., 943.

Ethyl α-cyano-1-methyl-Δ^2-*cyclo*hexene-3-acetate (HARDING and HAWORTH), T., 494.

Methyl α-cyano-α-1-methyl-Δ^2-*cyclo*hexene-2-propionate (HARDING and HAWORTH), T., 496.

$C_{12}H_{17}O_5N$ Mannoseanilide (IRVINE and MCNICOLL), T., 1453.

$C_{12}H_{18}ON_2$ Oxime of ethylidenexylidine (JONES and WHITE), T., 640.

$C_{12}H_{18}ON_4$ Cyanocaronesemicarbazide (CLARKE and LAPWORTH), T., 14.

$C_{12}H_{18}O_2N_2$ α- and β-Acetylcamphorquinonehydrazone (FORSTER and ZIMMERLI), T., 2168.

$C_{12}H_{18}O_4N_2$ Ethyl β-imino-α′-cyano-αα′-dimethylglutarate, α- and β-forms of (CAMPBELL and THORPE), T., 1309; P., 176.

2:3:4-Trimethoxy-β-phenylpropionylhydrazide, hydrochloride of (BARGER and EWINS), T., 2260.

$C_{12}H_{19}O_2N$ *d*-Camphorethylimide (EVANS), T., 2240.

$C_{12}H_{20}O_4S$ Ethyl camphor-β-sulphonate (EDMINSON and HILDITCH), T., 226.

$C_{12}H_{21}O_3N$ Ethyl α-camphoramic acid (WOOTTON), T., 413.

12 IV

$C_{12}H_5NCl_4S$ Tetrachlorothiodiphenylamine (PAGE and SMILES), T., 1118.

Trichlorophenazothionium chloride ($+H_2O$) (BRADY and SMILES), 1565.

$C_{12}H_6O_6N_4Br_4$ Substance, from 2:3:4:6-tetrabromoaniline and trinitrobenzene (SUDBOROUGH and BEARD), T., 782.

$C_{12}H_7O_6N_4Cl_3$ Substance, from *s*-trichloroaniline and trinitrobenzene (SUDBOROUGH and BEARD), T., 781.

$C_{12}H_7O_6N_4Br_3$ Substance, from 2:4:6-tribromoaniline and trinitrobenzene (Sudborough and Beard), T., 782.

$C_{12}H_8ON_3Br$ 4-Bromo-2-acetylnaphthylene-1-diazo-2-imide (Morgan and Godden), T., 1713.

$C_{12}H_8O_2Cl_2S$ *p*-Chlorophenol sulphide (Gazdar and Smiles), T., 2252.

$C_{12}H_8O_3Cl_2S$ *o*- and *p*-Chlorophenol sulphoxide (Gazdar and Smiles), T. 2251.

$C_{12}H_8O_6N_4Cl_2$ Substance, from 2:4-dichloroaniline and trinitrobenzene (Sudborough and Beard), T., 781.

$C_{12}H_8O_6N_4Br_2$ Substance, from 2:4- and 2:6-dibromoaniline and trinitrobenzene (Sudborough and Beard), T., 782.

$C_{12}H_8NBrS$ Bromothiodiphenylamine (Page and Smiles), T., 1118.

$C_{12}H_9ONS$ Phenazothionium hydroxide, intramolecular rearrangement ot the halides of (Page and Smiles), T., 1112 ; P., 133.

$C_{12}H_9O_3N_3S$ 1-Phenyl-1:2:3-benzotriazole-5-sulphonic acid (Schwalbe and Wolff), P., 340.

$C_{12}H_9O_6NS_2$ Carbazoledisulphonic acid (Schwalbe and Wolff), P., 340.

$C_{12}H_9O_6N_4Cl$ Substance, from *o*-, *m*- and *p*-chloroaniline and trinitrobenzene (Sudborough and Beard), T., 781.

$C_{12}H_9O_6N_4Br$ Substance, from *o*-, *m*- and *p*-bromoaniline and trinitrobenzene (Sudborough and Beard), T., 781.

$C_{12}H_{10}O_6N_2S_2$ Aminocarbazoledisulphonic acid (Schwalbe and Wolff), P., 340.

$C_{12}H_{11}O_4N_3S_2$ Carbazoledisulphonamide (Schwalbe and Wolff), P., 340.

$C_{12}H_{13}O_5NBr_2$ Methyl αβ-dibromo-5-nitro-2-ethoxy-β-phenylpropionate (Clayton), T., 2110.

$C_{12}H_{18}N_6Cl_2Fe$ Hexamethylferrocyanogen chloride (Hartley), T., 1729.

12 V

$C_{12}H_5ONCl_4S$ Tetrachlorodiphenylamine *o*-sulphoxide (Brady and Smiles), T., 1560.

Tetrachlorophenazothionium hydroxide ($+H_2O$) (Brady and Smiles), T., 1562.

$C_{12}H_6ONCl_3S$ Trichlorodiphenylamine *o*-sulphoxide, and its hydrochloride (Brady and Smiles), T., 1564.

$C_{12}H_6O_5N_2ClS$ Chlorodinitrodiphenylamine sulphoxide (Page and Smiles), T., 1116.

$C_{12}H_6O_7N_2Cl_2S$ *p*-Chloronitrophenol sulphoxide (Gazdar and Smiles), T., 2252.

$C_{12}H_7O_4NCl_2S_2$ Carbazoledisulphonyl chloride (Schwalbe and Wolff), P., 340.

$C_{12}H_{18}O_4N_6SFe$ Hexamethylferrocyanogen sulphate (+EtOH) (Hartley), T., 1729.

$C_{12}H_{18}N_6Cl_6FePt$ Platinichloride of substance, from potassium ferrocyanide and methyl sulphate (Hartley), T., 1072, 1725.

$C_{12}H_{20}O_8N_6S_2Fe$ Substance, from potassium ferrocyanide and methyl sulphate (Hartley), T., 1070, 1725.

C_{13} Group.

$C_{13}H_{10}O_3$ Substance, from the condensation of *cyclo*butan-1:3-dione in the presence of quinoline (Chick and Wilsmore), T., 1998 ; P., 217.

$C_{13}H_{11}N_5$ *p*-Triazobenzaldehydephenylhydrazone (Forster and Judd), T. 260.

$C_{13}H_{12}O_3$ 2:4-Dihydroxybenzhydrol, and its potassium salt (Pope and Howard), T., 80.

$C_{13}H_{14}O_2$ 6:7-Dimethoxy-1-methylnaphthalene (Luff, Perkin, and Robinson), T., 1140; P., 133.

$C_{13}H_{14}O_3$ Ethyl 2-methyl-1-hydrindone-2-carboxylate (Mitchell and Thorpe), T., 2274.

$C_{13}H_{14}O_6$ Methyl methyltrimesate (Simonsen), T., 1915.

$C_{13}H_{22}O_2$ Diethyl*apo*campholide (Shibata), T., 1242.

$C_{13}H_{22}O_4$ *n*-Propyl hydrogen camphorate (Edminson and Hilditch), T., 225.

Diethyl α-thujadicarboxylate (Thomson), T., 1514; P., 178.

13 III

$C_{13}H_8OS$ Thioxanthone, new syntheses of (Davis and Smiles), T., 1296; P., 93, 174; (Smiles), P., 342.

$C_{13}H_8O_2S$ Hydroxythioxanthone ($+\frac{1}{2}H_2O$) (Davis and Smiles), T., 1297; P., 174.

$C_{13}H_{10}ON_4$ *p*-Triazobenzylidene-*p*-aminophenol (Forster and Judd), T., 260; P., 28.

$C_{13}H_{10}O_2S$ Diphenylmethane *o*-sulphoxide, intramolecular rearrangements of (Hilditch and Smiles), P., 174.

$C_{13}H_{10}O_8N_4$ Substance, from *o*- and *p*-aminobenzoic acid and trinitrobenzene (Sudborough and Beard), T., 786.

$C_{13}H_{12}O_2N_2$ Ethyl α-*o*-dicyano-β-phenylpropionate (Mitchell and Thorpe), T., 2275.

$C_{13}H_{12}O_7N_4$ Substance, from *o*- and *p*-anisidine and trinitrobenzene (Sudborough and Beard), T., 785.

$C_{13}H_{12}NI$ *N*-Methyldiphenylamine hydriodide, mercuri-iodide of (Barnett and Smiles), T., 984.

$C_{13}H_{12}N_2S_2$ Immedial-indone, constitution of (Frank), T., 2014; P., 218.

$C_{13}H_{14}O_6N_6$ Substance, from triaminotoluene and trinitrobenzene (Sudborough and Beard), T., 787.

$C_{13}H_{15}O_2N$ α-Benzoyloxy*iso*hexonitrile (Davis), T., 951; P., 89.

$C_{13}H_{15}O_3N_3$ Semicarbazone of ethyl 1-hydrindone-2-carboxylate (Mitchell and Thorpe), T., 2274.

$C_{13}H_{15}O_4N_3$ Ethyl phenyltriazomalonate (Forster and Müller), T., 135; P., 4.

$C_{13}H_{15}O_5N$ Ethyl ether of ethyl 5-nitrocoumarinate (Clayton), T. 2107.

$C_{13}H_{16}O_5N_2$ Ethyl 4-cyano-2-keto-4-carbethoxytetrahydropyrrolidene-5-α-propionate (Campbell and Thorpe), T., 1314.

$C_{13}H_{17}O_2N_3$ Acetyl derivative of camphane-oxytriazine (Forster and Zimmerli), T., 2177.

$C_{13}H_{17}O_3N$ 3-Ethoxy-1:1-dimethyl-Δ^3-*cyclo*hexenylidene-5-cyanoacetic, acid (Crossley and Gilling), T., 531.

Ethyl 3-hydroxy-1:1-dimethyl-Δ^3-*cyclo*hexenylidene-5-cyanoacetate, and its silver salt (Crossley and Gilling), T., 527.

$C_{13}H_{17}O_4N_3$ Ethyl 2-imino-4-cyano-4-carbethoxytetrahydropyrrolidene-5-α-propionate (Campbell and Thorpe), T., 1313.

$C_{13}H_{18}O_4N_2$ Ethyl β-imino-α-cyano-1-carbethoxy-β-*cyclo*butyl-1-propionate (Campbell and Thorpe), T., 2422.

$C_{13}H_{19}ON$ α- and β-isomeride, from ψ-cumidine and acetaldehyde (Jones and White), T., 643.

$C_{13}H_{19}O_9N$ Gynocardin, and its sodium salt (Moore and Tutin), T., 1285; P., 182.

$C_{13}H_{21}O_2N$ Camphor-*n*-propylimide (Wootton), T., 415.

$C_{13}H_{21}O_{3}N$ Allyl-α-camphoramic acid (Wootton), T., 413.

$C_{13}H_{23}O_{3}N$ *n*-Propyl-α-camphoramic acid (Wootton), T., 413.

13 IV

$C_{13}H_{9}O_{5}N_{3}S$ Dinitro-*N*-methylphenazothionium hydrate (Barnett and Smiles), T., 191.

$C_{13}H_{9}O_{8}N_{4}K$ Substance, from potassium *o*-, *m*-, and *p*-aminobenzoate and trinitrobenzene (Sudborough and Beard), T., 786.

$C_{13}H_{10}O_{4}N_{6}S_{2}$ Methanedisulphonylbis-*p*-phenylenediazoimide (Morgan, Pickard, and Micklethwait), T., 60.

$C_{13}H_{10}NClS$ Chloro-*N*-methylthiodiphenylamine (Page and Smiles), T., 1116.

$C_{13}H_{11}ONS$ *N*-Methyldiphenylamine *o*-sulphoxide (Barnett and Smiles), T., 188.

N-Methylphenazothionium, platinichloride of (Barnett and Smiles), T., 189.

$C_{13}H_{11}O_{2}N_{3}S$ Toluene-ω-sulphonyl-*p*-phenylenediazoimide (Morgan and Pickard), T., 57.

$C_{13}H_{12}O_{4}N_{2}S$ Toluene-ω-sulphonyl-*p*-nitroaniline (Morgan and Pickard), T., 56.

$C_{13}H_{12}O_{8}N_{4}S_{2}$ Methanedisulphonylbis-*p*-nitroaniline (Morgan, Pickard, and Micklethwait), T., 58.

$C_{13}H_{12}O_{10}N_{8}S_{2}$ Methanedisulphonylbis-*p*-aminobenzenediazonium nitrate (Morgan, Pickard, and Micklethwait), T., 58.

$C_{13}H_{12}NIS$ *S*-Methyldiphenylamine-*o*-sulphonium iodide, mercuri-iodide of (Barnett and Smiles), T., 983.

$C_{13}H_{13}ONS$ *S*-Methylphenazothionium hydroxide, hydrochloride and platinichloride of (Barnett and Smiles), T., 986.

$C_{13}H_{14}O_{2}N_{2}S$ Toluene-ω-sulphonyl-*p*-phenylenediamine (Morgan and Pickard), T., 56.

$C_{13}H_{15}O_{5}N_{2}Ag$ Silver compound of ethyl 4-cyano-2-keto-4-carbethoxytetrahydropyrrolidene-5-α-propionate (Campbell and Thorpe), T., 1314.

$C_{13}H_{15}O_{5}N_{2}K$ Potassium compound of ethyl 4-cyano-2-keto-4-carbethoxytetrahydropyrrolidene-5-α-propionate (Campbell and Thorpe), T., 1314.

$C_{13}H_{16}O_{4}N_{4}S_{2}$ Methanedisulphonylbis-*p*-phenylenediamine (Morgan, Pickard, and Micklethwait), T., 58.

13 V

$C_{13}H.O_{5}N_{3}ClS$ Chlorodinitro-*N*-methyldiphenylamine *o*-sulphoxide (Page and Smiles), T., 1117.

$C_{13}H_{12}O_{4}N_{6}Cl_{2}S_{2}$ Methanedisulphonylbis-*p*-aminobenzenediazonium chloride (Morgan, Pickard, and Micklethwait), T., 58.

C_{14} Group.

$C_{14}H_{16}$ Tetramethylnaphthalene, absorption spectrum of (Homer and Purvis), T., 280; P., 5.

14 II

$C_{14}H_{6}Cl_{8}$ 3:4:3′:4′-Tetrachlorotolane tetrachloride (Kenner and Witham), T., 1964.

$C_{14}H_{8}O_{2}$ Phenanthraquinone, condensations of, with ethyl malonate and ethyl acetoacetate (Richards), T., 1456; P., 195.

$C_{14}H_8Cl_2$ 4:4′-Dichlorotolane (Kenner and Witham), T., 1965 ; P., 219.

$C_{14}H_8Cl_4$ *cis*- and *trans*-4:4′-Dichlorotolane dichloride (Kenner and Witham), T., 1964 ; P., 219.

$C_{14}H_8Cl_6$ 4:4′-Dichlorotolane tetrachloride (Kenner and Witham), T., 1963 ; P., 219.

$C_{14}H_{12}O_2$ Benzoin, substituted indoles from (Richards), T., 977 ; P., 92.
  l-Benzoin, optically active glycols from (McKenzie and Wren), T., 473 ; P., 54.

$C_{14}H_{12}O_6$ Substance, from red clover flowers (Power and Salway), T., 243 ; P., 20.

$C_{14}H_{14}O_4$ 2:4-Dihydroxy-4′-methoxybenzhydrol, and its dipotassium salt (Pope and Howard), T., 972 ; P., 88.

$C_{14}H_{14}O_8$ Methyl mellophanate (Bamford and Simonsen), T., 1909.

$C_{14}H_{14}S_2$ Benzyl disulphide (Smythe and Forster), T., 1196.

$C_{14}H_{14}S_3$ Benzyl trisulphide, and its additive compound with silver nitrate (Smythe and Forster), T., 1196 ; P., 135.

$C_{14}H_{14}S_4$ Benzyl tetrasulphide (Smythe and Forster), T., 1198 ; P., 136.

$C_{14}H_{15}N$ α-Phenyl-Δ^1-*cyclo*hexene-1-acetonitrile (Harding and Haworth), T., 497.

$C_{14}H_{16}O_3$ Piperonylidenepinacoline (Boon and Wilson), T., 1753 ; P., 208.

$C_{14}H_{16}O_6$ Acetoxydiacetyldimethoxybenzene (Tutin and Caton), T., 2066.

$C_{14}H_{20}O_5$ Ethyl 2:3:4-trimethoxy-β-phenylpropionate (Barger and Ewins), T., 2259.

$C_{14}H_{22}O$ 1:4′-Dimethyl-3-*cyclo*hexylidene*cyclo*hexan-4-one (Luff and Perkin), T., 2155.

$C_{14}H_{24}O_2$ Diethylcampholide (Shibata), T., 1241.

$C_{14}H_{24}O_3$ Methyl 1:2:3-trimethyl-3-*iso*butyryl*cyclo*pentane-1-carboxylate (Shibata), T., 1244 ; P., 142.

$C_{14}H_{24}O_4$ *n*-Butyl hydrogen camphorate (Edminson and Hilditch), T., 226.

$C_{14}H_{24}O_6$ Ethyl pentane-$\alpha\beta\delta$-tricarboxylate (Hope and Perkin), P., 178.
  Ethyl *iso*pentane-$\alpha\beta\delta$-tricarboxylate (Hope and Perkin), P., 179.

14 III

$C_{14}H_6O_2Cl_2$ 1:4-Dichloroanthraquinone (Walsh and Weizmann), T., 687 ; P., 61.

$C_{14}H_8O_2Cl_2$ 4:4′-Dichlorobenzil (Kenner and Witham), T., 1967.

$C_{14}H_9O_2N$ 2-Phenyl-1:3-benzoxazine-4-one (Titherley), T., 200 ; P., 9.

$C_{14}H_{10}OS$ Methylthioxanthone (Davis and Smiles), T., 1297 ; P., 174.

$C_{14}H_{10}O_2N_4$ Benzoyl derivative of *p*-triazobenz-*anti*-aldoxime (Forster and Judd), T., 259.

$C_{14}H_{10}O_2S$ Methoxythioxanthone (Davis and Smiles), T., 1297 ; P., 174.

$C_{14}H_{10}O_6S_2$ Di-*o*-carboxyphenyl disulphoxide (Hilditch), T., 2591.

$C_{14}H_{11}O_2N$ Dibenzamide, action of phosphorus pentachloride on (Titherley and Worrall), T., 839 ; P., 93.

$C_{14}H_{12}O_2S_2$ Ditolylene *p*-disulphoxide (Hilditch), T., 2591.

$C_{14}H_{12}O_7N_4$ Substance, from *p*-aminoacetophenone and trinitrobenzene (Sudborough and Beard), T., 786.

$C_{14}H_{12}O_8N_4$ Substance, from methyl *o*- and *p*-aminobenzoate and trinitrobenzene (Sudborough and Beard), T., 785.

$C_{14}H_{12}N_5Br$ Triazoacetophenonebromophenylhydrazone (Forster and Müller), T., 141.

$C_{14}H_{13}O_3N_3$ *o*-, *m*-, and *p*-Nitrobenzeneazophenetole (Baly, Tuck, and Marsden), T., 1501.

2-Nitro-4′-acetylbenzidine (Cain and May), T., 725.

Phenylhydrazone of 5-nitro-4-methylsalicylaldehyde (Clayton), T., 1407.

$C_{14}H_{14}O_2S$ *p*-Cresol sulphide (Gazdar and Smiles), T., 2250.

$C_{14}H_{14}O_3S$ *p*-Cresol *m*-sulphoxide (Gazdar and Smiles), T., 2248.

$C_{14}H_{14}O_5N_2$ Substance, from ethyl 1-cyano*cyclo*propane-1-carboxylate (Mitchell and Thorpe), T., 1001.

$C_{14}H_{15}O_3N$ Ethyl *o*-cyano-*α*-benzylacetoacetate (Mitchell and Thorpe), T., 2278.

$C_{14}H_{15}O_3Br$ Piperonylidenepinacoline monobromide (Boon and Wilson), T., 1753; P., 208.

$C_{14}H_{16}O_3Br_2$ Piperonylidenepinacoline dibromide (Boon and Wilson), T., 1754; P., 208.

$C_{14}H_{17}O_3N$ Oxime of piperonylidenepinacoline (Boon and Wilson), T., 1756; P., 208.

$C_{14}H_{17}O_3N_3$ Semicarbazone of ethyl 2-methyl-1-hydrindone-2-carboxylate (Mitchell and Thorpe), T., 2275.

$C_{14}H_{18}O_5N_2$ Ethyl 4-cyano-2-keto-4-carbethoxy-1-methyltetrahydropyrrolidene-5-*α*-propionate (Campbell and Thorpe), T., 1315.

$C_{14}H_{19}O_3N$ Ethyl 3-methoxy-1:1-dimethyl-Δ^3-*cyclo*hexenylidene-5-cyanoacetate, two stereoisomides (Crossley and Gilling), T., 528.

$C_{14}H_{23}ON$ Oxime of 1:4′-dimethyl-3-*cyclo*hexylidene*cyclo*hexan-4-one (Luff and Perkin), T., 2156.

$C_{14}H_{23}O_2N$ Camphor-*n*-butylimide (Wootton), T., 415.

$C_{14}H_{24}O_3S_2$ Camphoryl *n*-butyl-*β*-disulphoxide (Hilditch), T., 1098 P., 96.

$C_{14}H_{25}O_2N$ Carpaine, constitution of (Barger), T., 466; P., 53.

$C_{14}H_{25}O_3N$ *n*-Butyl-*α*-camphoramic acid (Wootton), T., 413.

$C_{14}H_{27}O_3N$ Carpamic acid, and its hydrochloride (Barger), T., 469; P. 53.

14 IV

$C_{14}H_5O_4NCl_2$ 1:4-Dichloro-5-nitroanthraquinone (Walsh and Weizmann), T., 687.

$C_{14}H_6O_5Cl_2S$ 1:4-Dichloroanthraquinone-6-sulphonic acid, sodium salt of (Walsh and Weizmann), T., 688.

$C_{14}H_7O_2NCl_2$ 1:4-Dichloro-5-aminoanthraquinone (Walsh and Weizmann), T., 687.

$C_{14}H_8O_2NCl$ 6-Chloro-2-phenyl-1:3-benzoxazine-4-one (Titherley and Hughes), T., 1376; P., 175.

$C_{14}H_8O_2NBr$ 6-Bromo-2-phenyl-1:3-benzoxazine-4-one (Hughes and Titherley), P., 344.

$C_{14}H_{10}ONCl$ *α*-Chloro-*N*-benzoylbenzimide, preparation of, from dibenzamide (Titherley and Worrall), T., 840; P., 98.

$C_{14}H_{10}O_2NCl$ *syn*-Benzylidene-5-chlorosalicylamide (Titherley and Hughes), T., 1376; P., 175.

6-Chloro-2-phenyldihydro-1:3-benzoxazine-4-one (Titherley and Hughes), T., 1374; P., 175.

$C_{14}H_{10}O_2NBr$ *syn*-Benzylidene-5-bromosalicylamide (Hughes and Titherley), P., 344.

6-Bromo-2-phenyldihydro-1:3-benzoxazine-4-one (Hughes and Titherley), P., 344.

$C_{14}H_{10}O_3NCl$ *O*- and *N*-Benzoyl-5-chlorosalicylamide (Titherley and Hughes), T., 1380; P., 175.

$C_{14}H_{10}O_3NBr$ *O*-Benzoyl-5-bromosalicylamide (Hughes and Titherley), P., 344.

N-Benzoyl-5-bromosalicylamide (Hughes and Titherley), P., 344.

$C_{14}H_{11}O_9NS_2$ Dicarboxybenzenesulphohydroximic acid (Davis and Smiles), T., 1295.

$C_{14}H_{12}ONCl$ Diphenylchloroacetamide (Clarke), T., 429.

$C_{14}H_{12}ON_2Cl_2$ 2:2′ and 3:3′-Dichloroacetylbenzidine (Cain and May), T., 723.

$C_{14}H_{12}O_6N_2S$ Nitro-*p*-cresol sulphide (Gazdar and Smiles), T., 2251.

$C_{14}H_{12}O_7N_2S$ Nitro-*p*-cresol sulphoxide (Gazdar and Smiles), T., 2250.

$C_{14}H_{14}NIS$ *N*-*S*-Dimethyldiphenylamine-*o*-sulphonium iodide, mercuriiodide of (Barnett and Smiles), T., 985.

$C_{14}H_{15}O_3N_3S$ *p*-Dimethylaminoazobenzene-*p*-sulphonic acid, sodium salt, (*methyl orange*) colour changes of, in acid solution (Tizard), T., 2477 ; P., 225.

$C_{14}H_{23}O_3NCl_2$ Substance, from carpaine hydrochloride and chlorine (Barger) T., 472 ; P., 53.

14 V

$C_{14}H_{24}O_8N_6S_2Fe$ Hexamethyl ferrocyanogen methyl sulphate (Hartley), T., 1726 ; P., 210.

C_{15} Group.

$C_{15}H_{10}O_6$ Substance, from red clover flowers (Power and Salway), T., 239 ; P., 20.

$C_{15}H_{12}O_6$ Eriodictyol (2:4:6-*trihydroxyphenyl 3:4-dihydroxystyryl ketone*) (Tutin), T., 2058 ; P., 222.

$C_{15}H_{16}O_2$ *l*-$\alpha\beta$-Dihydroxy-$\alpha\beta$-diphenylpropane (McKenzie and Wren), T., 477.

$C_{15}H_{16}O_3$ 2:4-Dimethoxybenzhydrol (Pope and Howard), T., 81.

$C_{15}H_{17}N$ α-Phenyl-1-methyl-Δ^3-*cyclo*hexene-4-acetonitrile (Harding and Haworth), T., 498.

$C_{15}H_{26}O_4$ Di-*n*-propyl α-thujadicarboxylate (Thomson), T., 1514 ; P., 178.

$C_{15}H_{29}N_3$ Substance, from ethylidenexylidine and phenylbenzylhydrazine (Jones and White), T., 641.

15 III

$C_{15}H_8ON_2$ Ketohydrindenophenazine (Ruhemann), T., 1449.

$C_{15}H_8O_3Cl_2$ 1:4-Dichloro-8-hydroxy-5-methylanthraquinone (Walsh and Weizmann), T., 690.

1:4-Dichloro-6 (or 5-) -hydroxy-5 (or 6-) -methylanthraquinone (Walsh and Weizmann), T., 691.

$C_{15}H_{10}O_3N_4$ 5-*p*-Nitrobenzeneazo-8-hydroxyquinoline, and its hydrochloride and sodium salt (Fox), T., 1343.

$C_{15}H_{10}O_4Cl_2$ 3:6-Dichloro-5′ (or 6′-) -hydroxy-2-*o* (or *m*-) -toluoylbenzoic acid, and its sodium salt (Walsh and Weizmann), T., 689.

3:6-Dichloro-3′ (or 2′-) -hydroxy-2-*o* (or *m*-) toluoylbenzoic acid (Walsh and Weizmann), T., 691.

$C_{15}H_{10}O_6N_4$ Substance, from quinoline and trinitrobenzene (Sudborough and Beard), T., 794.

Substance, from *iso*quinoline and trinitrobenzene (Sudborough and Beard), T., 795.

$C_{15}H_{11}ON_3$ Quinolineazophenol, and its hydrochlorides (Fox), T., 1346.

5-Benzeneazo-8-hydroxyquinoline, and its salts, (Fox), T., 1339 ; P., 177.

$C_{15}H_{11}O_2N$ ω-Amino-*o*-hydroxy-acetophenone, hydriodide (Tutin), T., 2518 ; P., 245.

$C_{15}H_{11}O_7N_5$ Substance, from 3-phenylpyrazolone and trinitrobenzene (SUDBOROUGH and BEARD), T., 797.

$C_{15}H_{12}ON_4$ 5-*p*-Aminobenzeneazo-8-hydroxyquinoline, and its salts (FOX), T., 1343.

$C_{15}H_{12}O_6N_4$ Substance, from α-methylindole and trinitrobenzene (SUDBOROUGH and BEARD), T., 796.

$C_{15}H_{13}O_4N$ α-Benzoylamino-*op*-dihydroxyacetophenone (TUTIN), T., 2516.

$C_{15}H_{14}O_6N_4$ Substance, from tetrahydroquinoline and trinitrobenzene (SUDBOROUGH and BEARD), T., 796.

$C_{15}H_{14}O_7N_4$ Substance, from trinitrobenzene and dimethyl-*p*-aminobenzaldehyde (SUDBOROUGH and BEARD), T., 791.

$C_{15}H_{14}O_8N_4$ Substance, from ethyl *o*- and *p*-aminobenzoate and trinitrobenzene (SUDBOROUGH and BEARD), T., 785.

$C_{15}H_{15}O_2N_3$ Dimethylaminoazobenzene-*o*-carboxylic acid (*methyl red*), colour changes of, in acid solution (TIZARD), T., 2477 ; P., 225.

$C_{15}H_{15}O_6N_5$ Substance, from acetonephenylhydrazone and trinitrobenzene (SUDBOROUGH and BEARD), T., 793.

$C_{15}H_{15}NS$ Phenylethylthiobenzamide (RUSSELL), T., 957.

$C_{15}H_{17}O_3N$ Benzenesulphonyl-*p*-methoxyphenylethylamine (WALPOLE), T., 946.

Benzoyloscine, resolution of (TUTIN), T., 1793 ; P., 215.

Benzoyl-*d*-oscine, and its salts (TUTIN), T., 1796 ; P., 215.

$C_{15}H_{17}O_4N$ Ethyl *o*-cyanobenzylmalonate (MITCHELL and THORPE), T., 2270 ; P., 249.

$C_{15}H_{19}O_2N$ α-Benzoyloxyoctonitrile (DAVIS), T., 951 ; P., 89.

$C_{15}H_{19}O_5N$ 3:4-Diacetoxy-*N*-acetylphenylethylmethylamine (PYMAN), T., 273.

$C_{15}H_{21}O_3N$ Ethyl 3-ethoxy-1:1-dimethyl-Δ^3-*cyclo*hexenylidene-5-cyanoacetate, two stereoisomerides (CROSSLEY and GILLING), T., 529.

$C_{15}H_{23}O_4N$ Trimethyl rhamnoseanilide (IRVINE and McNICOLL), T., 1455.

$C_{15}H_{23}O_6N$ Ethyl β-cyanopentane-αβδ-tricarboxylate (HOPE and PERKIN), P., 178.

Ethyl β-cyano*iso*pentane-αβδ-tricarboxylate (HOPE and PERKIN), P., 178.

$C_{15}H_{25}O_2N$ Camphor-*n*-amylimide (WOOTTON), T., 415.

$C_{15}H_{27}O_3N$ *n*-Amyl-α-camphoramic acid (WOOTTON), T., 413.

15 IV

$C_{15}H_8O_2N_2Cl_6$ 2:4:6:2′:4′:6′-Hexachloromalonanilide (CHATTAWAY and MASON), T., 342.

$C_{15}H_8O_2N_2Br_6$ 2:4:6:2′:4′:6′-Hexabromomalonanilide (CHATTAWAY and MASON), T., 344.

$C_{15}H_9O_4Cl_2Br$ 3:6-Dichlorobromo-5′ (or 6′-) -hydroxy-2-*o* (or *m*-) -toluoylbenzoic acid (WALSH and WEIZMANN), T., 689.

$C_{15}H_{10}ON_3Br$ 5-*p*-Bromobenzeneazo-8-hydroxyquinoline, and its hydrochlorides (FOX), T., 1342.

$C_{15}H_{10}O_2N_2Cl_4$ 2:4:2′:4′-Tetrachloromalonanilide (CHATTAWAY and MASON), T., 342.

$C_{15}H_{10}O_2N_2Br_4$ 2:4:2′:4′-Tetrabromomalonanilide (CHATTAWAY and MASON), T., 344.

$C_{15}H_{12}O_2N_2Cl_2$ *pp*-Dichloromalonanilide (CHATTAWAY and MASON), T., 340.

$C_{15}H_{12}O_2N_2Br_2$ *pp*-Dibromomalonanilide (CHATTAWAY and MASON), T., 343.

$C_{15}H_{14}O_5N_2S$ Phenetoleazobenzaldehydesulphonic acid, metallic salts of, (GREEN and SEN), T., 2243.

$C_{15}H_{17}O_3NS$ Benzenesulphonyl-*p*-hydroxyphenylethylmethylamine (WALPOLE), T., 947.

C_{16} Group.

$C_{16}H_{10}O_2$ 2-Keto-4:5-diphenylene-2:3-dihydrofuran (Richards), T., 1458; P., 195.

$C_{16}H_{10}O_6$ Trifolitin (Power and Salway), T., 240; P., 20.

$C_{16}H_{10}O_7$ Substance, from red clover flowers (Power and Salway), T., 236; P., 20.

$C_{16}H_{12}O$ 3-Phenyl-1-naphthol (Ruhemann), T., 461.

$C_{16}H_{12}O_3$ 9-Hydroxy-10-phenanthrylacetic acid, and its barium and sodium salts (Richards), T., 1458; P., 195.

$C_{16}H_{12}O_4$ Pratol, from red clover flowers (Power and Salway), T., 233; P., 20.

$C_{16}H_{12}O_5$ Dura-santalin (Perkin), T., 223; P., 23.

$C_{16}H_{12}O_7$ *iso*Rhamnetin, in red clover flowers (Power and Salway), T., 244; P., 20.

$C_{16}H_{12}N_2$ 2:5-Diphenylpyrazine, salts of (Tutin and Caton), T., 2530; P., 245.

2:6-Diphenylpyrazine, salts of (Tutin), T., 2501; (Tutin and Caton), T., 2531; P., 245.

$C_{16}H_{13}N_3$ Phenylhydrazone of 2-cyano-1-hydrindone (Mitchell and Thorpe), T., 2278.

$C_{16}H_{14}O_2$ β-Benzylcinnamic acid (Ruhemann), T., 460.

Phenyl *o*-methoxystyryl ketone (*o-methoxybenzylideneacetophenone*) (Stobbe and Wilson), T., 1724; P., 206.

$C_{16}H_{14}O_3$ Benzoyl derivative of methyl *p*-coumarate (Power and Salway), T., 235.

$C_{16}H_{14}O_6$ Homoeriodictyol (2:4:6-*trihydroxyphenyl* 4-*hydroxy*-3-*methoxystyryl ketone*) (Tutin), T., 2059; P., 222.

Hesperitin (2:4:6-*trihydroxyphenyl* β-*hydroxy*-4-*methoxystyryl ketone*) (Tutin), T., 2060; P., 222.

Monomethyleriodictyol (2:6-*dihydroxy*-4-*methoxyphenyl* 3:4-*dihydroxystyryl ketone*) (Tutin), T., 2059.

$C_{16}H_{16}O_2$ β-Phenyl-β-benzylpropionic acid, and its silver salt (Ruhemann), T., 460.

$C_{16}H_{16}N_2$ Phenylhydrazone of 2-methyl-1-hydrindone (Mitchell and Thorpe), T., 2275.

$C_{16}H_{18}O_2$ Dimethoxy-*p*-tolylphenylmethane (Mackenzie), P., 170.

l-αβ-Dihydroxy-αβ-diphenylbutane (McKenzie and Wren), T., 479.

$C_{16}H_{18}O_6$ Ethyl methyltrimesate (Simonsen), T., 1913.

$C_{16}H_{20}O_4$ Phenyl hydrogen camphorate (Edminson and Hilditch), T., 227.

α- and β-Ethoxypiperonylidenepinacoline (Boon and Wilson), T., 1755; P., 208.

Benzyl α-thujadicarboxylate (Thomson), T., 1515; P., 178.

16 III

$C_{16}H_{10}O_2N_2$ Indirubin (Bloxam and Perkin), T., 1460; P., 168.

$C_{16}H_{10}O_3Cl_2$ 1:4-Dichloro-7 (or 5)-methoxy-5 (or 7)-methylanthraquinone (Walsh and Weizmann), T., 692.

$C_{16}H_{11}O_5N$ ω-Phthalimino-*op*-dihydroxyacetophenone (Tutin), T., 2517.

$C_{16}H_{11}O_6N_5$ Substance, from β-imino-α-cyanohydrindene and trinitrobenzene (Sudborough and Beard), T., 790.

$C_{16}H_{11}O_8N_5$ Substance, from α-nitro-β-naphthylamine and trinitrobenzene (Sudborough and Beard), T., 785.

$C_{16}H_{12}O_2N_2$ *oo'*-Dihydroxy-2:5-diphenylpyrazine (Tutin), T., 2518; P., 245.

pp'-Dihydroxy-2:6-diphenylpyrazine, and its salts (Tutin), T., 2523; P., 244.

$C_{16}H_{12}O_3N_2$ Substance, from triketohydrindene and benzamidine (RUHEMANN), T., 2029 ; P., 235.

$C_{16}H_{12}O_4N_2$ *oo'pp'*-Tetrahydroxy-2:5-diphenylpyrazine, and its sulphates (TUTIN), T., 2514 ; P., 245.

$C_{16}H_{12}O_4Cl_2$ 3:6-Dichloro-4′ (or 2′)-methoxy-2-*o*-(or *p*)-toluoylbenzoic acid (WALSH and WEIZMANN), T., 691.

$C_{16}H_{13}ON_3$ 5-*p*-Tolueneazo-8-hydroxyquinoline, and its salts (FOX), T., 1341.

$C_{16}H_{13}O_2N$ 1-Hydrindone-2-carbanilide (MITCHELL and THORPE), T., 2274.

$C_{16}H_{13}O_6N$ ω-Phthalamino-*op*-dihydroxyacetophenone, (TUTIN), T., 2517.

$C_{16}H_{13}O_6N_5$ Substance, from *o*-amino-*p*-toluquinone and trinitrobenzene (SUDBOROUGH and BEARD), T., 796.

Substance, from trinitrobenzene and naphthylenediamine (1:2-, 1:4-, 1-5-, and 1:8-) (SUDBOROUGH and BEARD), T., 787.

$C_{16}H_{13}O_7N_5$ Substance, from 1-phenyl-3-methylpyrazolone and trinitrobenzene (SUDBOROUGH and BEARD), T., 797.

$C_{16}H_{14}O_6N_4$ 2:2′-Dinitrodiacetylbenzidine (CAIN and MAY), T., 724.

$C_{16}H_{15}O_2N$ Diphenacylamine, hydriodide of (TUTIN), T., 2521 ; P., 244.

$C_{16}H_{15}O_4N$ *pp'*-Dihydroxydiphenacylamine, and its salts (TUTIN), T., 2522 ; P., 244.

$C_{16}H_{15}O_4N_3$ 2-Nitrodiacetylbenzidine (CAIN and MAY), T., 725.

$C_{16}H_{15}O_6N$ *mm'pp'*-Tetrahydroxydiphenacylamine, salts of (TUTIN), T., 2523 ; P., 244.

$C_{16}H_{16}O_6N_4$ Substance, from *ar*-tetrahydro-α-naphthylamine (SUDBOROUGH and BEARD), T., 786.

$C_{16}H_{16}O_{10}N_8$ Caffeine salt of 2:3:5-trinitro-4-acetylaminophenol (MELDOLA and KUNTZEN), T., 453.

$C_{16}H_{17}O_4N$ Narcissine and its hydrochloride (EWINS), T., 2406 ; P., 296.

$C_{16}H_{18}O_2N_2$ 4′-Acetyl-3-ethoxybenzidine (CAIN and MAY), T., 725.

$C_{16}H_{18}O_3N_2$ *p*-Azoxyphenetole, absorption of carbon dioxide by, relation between solubility and the physical state of the solvent in the (HOMFRAY), T., 1669 ; P., 197.

Acetyldianisidine (and + H_2O) (CAIN and MAY), T., 723.

$C_{16}H_{18}O_4N_2$ Camphor-3-nitrophenylimide (WOOTTON), T., 415.

$C_{16}H_{19}O_3N$ Laurepukine (ASTON), T., 1387 ; P., 11.

$C_{16}H_{19}O_6N_5$ Substance, from tetramethyl-*p*-phenylenediamine and trinitrobenzene (SUDBOROUGH and BEARD), T., 792.

$C_{16}H_{19}ClSi$ Dibenzylethylsilicyl chloride (CHALLENGER and KIPPING), T., 146.

$C_{16}H_{20}O_4S$ Phenyl camphor-β-sulphonate (EDMINSON and HILDITCH), T., 228.

$C_{16}H_{20}O_5N_2$ 3-Nitrophenyl-α-camphoramic acid (WOOTTON), T., 413.

$C_{16}H_{21}O_4N$ 4-Hydroxyphenyl-α-camphoramic acid (WOOTTON), T., 414.

$C_{16}H_{21}O_4Br$ Bromoethoxypiperonylidenepinacolin (BOON and WILSON), T., 1754.

$C_{16}H_{22}O_3N_2$ 3-Aminophenyl-α-camphoramic acid, and its hydrochloride (WOOTTON), T., 414.

$C_{16}H_{23}ON$ Δ^{a}-Noneno-*p*-toluidide (HARDING and WEIZMANN), T., 302.

$C_{16}H_{25}O_2N$ Camphorcarboxypiperidide (GLOVER and LOWRY), P., 163.

$C_{16}H_{25}O_5N$ Tetramethyl mannoseanilide (IRVINE and MCNICOLL), T., 1452

Tetramethyl galactoseanilide (IRVINE and MCNICOLL), T., 1454.

$C_{16}H_{27}O_2N$ Camphor-*n*-hexylimide (WOOTTON), T., 415.

$C_{16}H_{29}O_3N$ *n*-Hexyl-α-camphoramic acid (WOOTTON), T., 413.

$C_{16}H_{31}O_3N$ Ethyl carpamate, hydrochloride of (BARGER), T., 469.

16 IV

$C_{16}H_9O_3NCl_2$ 1:4-Dichloro-5-acetylaminoanthraquinone (Walsh and Weizmann), T., 688.

$C_{16}H_9O_4N_3S_2$ Dinitro-*S*-thienylphenazothionium hydroxide ($+\frac{1}{2}H_2O$) (Barnett and Smiles), T., 373.

$C_{16}H_{10}O_6N_4Br_2$ Substance, from 1:6-dibromo-2-naphthylamine and trinitrobenzene (Sudborough and Beard), T., 782.

$C_{16}H_{11}O_2N_3S$ 1-Benzenesulphonylnaphthylene-2-diazo-1-imide (Morgan and Godden), T., 1717.

2-Benzenesulphonylnaphthylene-1-diazo-2-imide (Morgan and Godden), T., 1715.

Benzenesulphonylnaphthylene-2:3-diazoimide (Morgan and Godden), T., 1718.

$C_{16}H_{11}O_4NCl_2$ 1:4-Dichloro-5-aminoanthraquinone acetate (Walsh and Weizmann), T., 688.

$C_{16}H_{11}O_6N_3S$ Benzenesulphonyl-2:4-dinitro-α-naphthylamine (Morgan and Godden), T., 1715.

$C_{16}H_{11}O_6N_4Br$ Substance, from 4-bromo-1-naphthylamine and trinitrobenzene (Sudborough and Beard), T., 782.

Substance, from α-bromo-β-naphthylamine and trinitrobenzene (Sudborough and Beard), T., 782.

$C_{16}H_{12}O_4N_2S$ Benzenesulphonyl-1-nitro-β-naphthylamine (Morgan and Godden), T., 1714.

$C_{16}H_{14}O_2N_2Cl_2$ 2:2′-Dichlorodiacetylbenzidine (Cain and May), T., 724.

$C_{16}H_{14}O_2N_2S$ 2-Benzenesulphonyl-1:2-naphthylenediamine (Morgan and Godden), T., 1714.

$C_{16}H_{14}O_4N_2Cl_2$ Tartarodi-*o*-, *m*-, and *p*-chloroanilide (Frankland and Twiss), T., 159.

$C_{16}H_{14}O_4N_2Br_2$ Tartarodi-*o*-, *m*-, and *p*-bromoanilide (Frankland and Twiss), T., 157.

$C_{16}H_{15}O_2N_3S$ 1-Benzenesulphonyl-1:2:4-triaminonaphthalene (Morgan and Godden), T., 1716.

$C_{16}H_{16}O_3NCl$ Phenylurethane of γ-chloro-β-hydroxy-α-phenoxypropane (Boyd and Marle), T., 1789; P., 209.

$C_{16}H_{18}O_2NCl$ Camphor-2-, 3-, and 4-chlorophenylimide (Wootton), T., 415.

$C_{16}H_{18}O_2NBr$ Camphor-2-, and 3-bromophenylimide (Wootton), T., 415.

$C_{16}H_{20}O_3NCl$ 2-, 3-, and 4-Chlorophenyl-α-camphoramic acid (Wootton), T., 415.

$C_{16}H_{20}O_3NBr$ 2-, and 3-Bromophenyl-α-camphoramic acid (Wootton), T., 415.

$C_{16}H_{24}O_2NBr$ Camphorcarboxybromopiperidide (Glover and Lowry), P. 163.

16 V

$C_{16}H_{10}O_2N_3BrS$ 2-Benzenesulphonyl-4-bromonaphthylene-1-diazo-2-imide (Morgan and Godden), T., 165.

1-Benzenesulphonyl-4-bromonaphthylene-2-diazo-1-imide (Morgan and Godden), T., 1712; P., 165.

$C_{16}H_{11}O_4N_2BrS$ Benzenesulphonyl-2-nitro-4-bromo-α-naphthylamine (Morgan and Godden), T., 1711.

$C_{16}H_{12}O_2NBrS$ Benzenesulphonyl-4-bromo-α-naphthylamine (Morgan and Godden), T., 1710.

$C_{16}H_{13}O_2N_2BrS$ 1-, and 2-Benzenesulphonyl-4-bromo-1:2-naphthylenediamine (Morgan and Godden), T., 1709; P., 165.

$C_{16}H_{32}O_{16}N_6S_4Fe$ Substance, from potassium ferrocyanide and methyl sulphate (Hartley), T., 1071, 1725.

C_{17} Group.

$C_{17}H_{12}O_2$ 2-Benzo-α-naphthol, and its salts (Edminson and Hilditch), T., 226.

$C_{17}H_{12}O_5$ Pratensol, from red clover flowers (Power and Salway). T., 238; P., 20.

$C_{17}H_{13}N_3$ 3-*p*-Tolyl-β-naphtha*iso*triazole (*2-p-tolylnaphthylene-1-diazo-2-imine*), (Morgan and Bramley), P., 151.

$C_{17}H_{14}O_4$ Chrysophanic acid dimethyl ether (Tutin and Clewer), T., 6.

$C_{17}H_{16}O_2$ ββ-Dibenzoylpropane (Smedley), T., 1492.

$C_{17}H_{16}O_5$ 2:4-Diacetoxybenzhydrol (Pope and Howard), T., 80.

$C_{17}H_{18}O_8$ Triethyl hydrogen prehnitate (Bamford and Simonsen), T., 1908.

$C_{17}H_{24}O_2$ Menthyl benzoate (Cohen and Dudley), T., 1750.

$C_{17}H_{30}O_4$ Di*iso*butyl α-thujadicarboxylate (Thomson), T., 1514; P., 178.

17 III

$C_{17}H_{10}OS$ Naphthathioxanthone (Davis and Smiles), T., 1298; P., 174.

$C_{17}H_{10}O_4Cl_2$ 1:4-Dichloro-8-acetoxy-5-methylanthraquinone (Walsh and Weizmann), T., 690.

$C_{17}H_{11}O_2N$ *O*-Benzoyl-2-cyano-1-hydrindone (Mitchell and Thorpe), T., 2278.

$C_{17}H_{11}O_5N_3$ *o*-, and *p*-Nitro-*o*-carboxybenzene-4-azo-α-naphthol (Baly, Tuck, and Marsden), T., 1501.

$C_{17}H_{12}ON_4$ Benzoyl-1-aminonaphthyl-4-azoimide (Morgan and Couzens), T., 1697.

$C_{17}H_{12}ON_6$ Benzoyl-1-aminonaphthalene-4-diazonium azide (Morgan and Couzens), T., 1697.

$C_{17}H_{12}O_7N_4$ Azo derivative of 2:5-dinitro-1-methoxy-3:4-quinonediazide (Meldola and Reverdin), T., 1206.

Substance, from formo-α- and β-naphthalide and trinitrobenzene (Sudborough and Beard), T., 790.

$C_{17}H_{13}O_2N_3$ Quinolineazophenyl acetate (Fox), T., 1346.

$C_{17}H_{13}O_4N$ ω-Phthalimino-*o*-methoxyacetophenone (Tutin), T., 2517.

ω-Phthalimino-*p*-methoxyacetophenone (Tutin), T., 2508.

$C_{17}H_{14}O_2N_4$ 5-*p*-Acetylaminobenzeneazo-8-hydroxyquinoline, and its sodium salt (Fox), T., 1343.

$C_{17}H_{15}ON_3$ Quinolineazophenetole (Fox), T., 1347.

$C_{17}H_{15}O_2N_3$ 5-*p*-Ethoxybenzeneazo-8-hydroxyquinoline, and its sodium salt and hydrochloride (Fox), T., 1344.

Ethoxyquinolineazophenol (Fox), T., 1347.

$C_{17}H_{16}ON_2$ *p*-Dimethylaminoanilo-α-hydrindone (Ruhemann), T., 1446.

$C_{17}H_{17}O_3N$ Pukateine, and its salts (Aston), T., 1382; P., 11.

$C_{17}H_{17}O_4N$ Benzoyl derivative of β-3-methoxy-4:5-methylenedioxy-phenylethylamine (Salway), T., 1212.

$C_{17}H_{18}O_3N_2$ *l*-Methoxysuccindianilide (Purdie and Neave), T., 1520.

$C_{17}H_{19}O_3N$ 2-, 3-, and 4-Nitrobenzylidenecamphor (Wootton), T., 411, 412.

$C_{17}H_{20}ON_2$ Benzylidenecamphorquinonehydrazone (Forster and Zimmerli), T., 2170.

$C_{17}H_{20}O_2N_2$ αβ-Dibenzylaminopropionic acid, and its dihydrochloride (Frankland), T., 1688; P., 202.

Phenylhydrazone of 4:5-dimethoxy-*o*-methylacetophenone (Harding and Weizmann), T., 1128; P., 130.

α-Benzoylcamphorquinonehydrazone (Forster and Zimmerli), T., 2169.

$C_{17}H_{21}O_2N$ *d*-Camphorbenzylimide, preparation of (Evans), T., 2240.

Camphor *o*-, *m*-, and *p*-tolylimide (Wootton), T., 415.

$C_{17}H_{21}O_2N_3$ Camphorquinone-α- and β-phenylcarbamylhydrazone (Forster and Zimmerli), T., 2174; P., 245.

$C_{17}H_{23}O_2N$ Phenylurethane of Δ^3-*m*-menthenol (8) (Luff and Perkin), T., 2153.

Phenylurethane of Δ^3-*p*-menthenol (8) (Perkin and Wallach), T., 1433.

$C_{17}H_{23}O_3N$ *o*-, *m*-, and *p*-Tolyl-α-camphoramic acid (Wootton), T., 415.

Hyoscyamine, specific rotatory power of (Carr and Reynolds), T., 1328; P., 180.

17 IV

$C_{17}H_{11}ONS$ β-Aminonaphthathioxanthone, and its platinichloride (Davis and Smiles), T., 1299; P., 174.

$C_{17}H_{14}O_4N_2S_2$ Substance, from immedial-indone (Frank), T., 2045; P., 218.

$C_{17}H_{15}O_3N_3S$ Methanesulphonyl-*p*-aminobenzeneazo-β-naphthol (Morgan, Pickard, and Micklethwait), T., 63.

$C_{17}H_{18}O_3NCl$ Phenylurethanes of γ-chloro-β-hydroxy-α-*o*-, and *p*-tolyloxypropane (Boyd and Marle), T., 1790; P., 209.

C_{18} Group.

$C_{18}H_{13}N_3$ *oo*-Dicyano-ββ′-diphenyl*iso*butyronitrile (Mitchell and Thorpe), T., 2280.

$C_{18}H_{14}O_5$ Acetyl derivative of pratol (Power and Salway), T., 233.

$C_{18}H_{16}O_4$ *p*-Carbethoxydibenzoylmethane (Smedley), T., 1491.

$C_{18}H_{16}O_6$ *oo*-Dicarboxy-ββ′-diphenyl*iso*butyric acid (Mitchell and Thorpe), T., 2281.

$C_{18}H_{18}O_6$ Diacetyl derivative of 2:4-dihydroxy-4′-methoxybenzhydrol (Pope and Howard), T., 973.

$C_{18}H_{26}O_2$ Menthyl phenylacetate (Cohen and Dudley), T., 1749.

Menthyl *o*-, *m*-, and *p*-toluate (Cohen and Dudley), T., 1749.

$C_{18}H_{26}O_3$ Menthyl *o*-, *m*-, and *p*-methoxybenzoate (Cohen and Dudley), T., 1739.

18 III

$C_{18}H_{10}O_4N_2$ 2-*o*-Carboxybenzoylindonoglyoxaline, and its silver salt (Ruhemann), T., 1442.

$C_{18}H_{12}ON_4$ Quinolineazo-8-hydroxyquinoline, and its sodium salt and hydrochlorides (Fox), T., 1345.

$C_{18}H_{12}O_6N_4$ Substance, from carbazole and trinitrobenzene (Sudborough and Beard), T., 796.

$C_{18}H_{13}NS$ *N*-Phenylthiodiphenylamine (Barnett and Smiles), T., 364.

$C_{18}H_{15}O_5N$ ω-Phthalimino-*op*-dimethoxyacetophenone (Tutin), T., 2513.

$C_{18}H_{15}O_6N_7$ Substance, from 2:4-diaminoazobenzene and trinitrobenzene (Sudborough and Beard), T., 787.

$C_{18}H_{16}O_2N_2$ *pp*′-Dimethoxy-2:5-diphenylpyrazine, and its salts (Tutin), T., 2505; P., 244; (Tutin and Caton), T., 2531; P., 245.

pp′-Dimethoxy-2:6-diphenylpyrazine, and its salts (Tutin), T., 2506; P., 244; (Tutin and Caton), T., 2532; P., 245.

$C_{18}H_{16}O_7N_4$ Substance, from α-amino-β-naphthyl ethyl ether and trinitrobenzene (Sudborough and Beard), T., 787.

$C_{18}H_{16}O_8N_4$ Substance, from ethyl 2-aminoindene-3-carboxylate and trinitrobenzene (Sudborough and Beard), T., 788.

$C_{18}H_{17}O_3N$ 8-Methoxy-6:7-methylenedioxy-1-benzyl-3:4-dihydro*iso*quinoline, and its hydrochloride ($+2H_2O$) and picrate (Salway), T., 1214.

6-Methoxy-7:8-methylenedioxy-1-benzyl-3:4-dihydro*iso*quinoline, and its hydrochloride and picrate (Salway), T., 1215.

$C_{18}H_{18}O_2N_2$ Phenylhydrazone of ethyl 1-hydrindone-2-carboxylate (MITCHELL and THORPE), T., 2273.

$C_{18}H_{18}O_3N_2$ *cis*-Betrahydrofuran-2:5-dicarboxyldianilide (LE SUEUR and HAAS), T., 184.

$C_{18}H_{18}O_4N_2$ Acid diamide of *oo*-dicarboxy-*ββ′*-diphenyl*iso*butyric acid (MITCHELL and THORPE), T., 2281.

$C_{18}H_{18}O_8N_4$ Substance, from ethyl *β*-anilinocrotonate and trinitrobenzene (SUDBOROUGH and BEARD), T., 790.

$C_{18}H_{18}N_3Sb$ Tri-*p*-aminotriphenylstibine (MAY), P., 142.

$C_{18}H_{19}O_2N_3$ *β*-Benzyl-*γ*-benzylaminomethylhydantoin, and its hydrochloride (FRANKLAND), T., 1689 ; P., 203.

Benzoyl derivative of camphane-oxytriazine (FORSTER and ZIMMERLI), T., 2177.

$C_{18}H_{19}O_4N$ Phenylacetyl-*β*-3-methoxy-4:5-methylenedioxyphenylethylamine (SALWAY), T., 1213.

pp′-Dimethoxydiphenacylamine, hydrochloride of (TUTIN), T., 2507.

$C_{18}H_{20}O_3N_2$ Diacetyl-3-ethoxybenzidine (CAIN and MAY), T., 725.

$C_{18}H_{20}O_4N_2$ Phenylhydrazone of hydroxydiacetyldimethoxybenzene (TUTIN and CATON), T., 2066.

$C_{18}H_{21}O_3N_3$ *β*-Benzylamino-*α*-benzylcarbamidopropionic acid (FRANKLAND), T., 1689 ; P., 203.

$C_{18}H_{21}O_4N$ Hydroxycodeine, and its salts (DOBBIE and LAUDER), P., 339.

$C_{18}H_{24}O_4N_2$ Acetyl derivative of 3-amino-phenyl-*α*-camphoramic acid (WOOTTON), T., 414.

$C_{18}H_{25}O_4N$ 4-Ethoxyphenyl-*α*-camphoramic acid (WOOTTON), T., 415.

18 IV

$C_{18}H_{12}O_6N_3Sb$ Trinitrotriphenylstibine (MAY), P., 142.

$C_{18}H_{13}O_7N_4Br$ Acetyl derivative of substance, from *α*-bromo-*β*-naphthylamine and trinitrobenzene (SUDBOROUGH and BEARD), T., 782.

$C_{18}H_{14}O_8N_3Sb$ Trinitrophenylstibine dihydroxide, and its dichloride (MAY), T., 1958.

$C_{18}H_{15}O_4SSb$ Triphenylstibine sulphate (MAY), T., 1958.

$C_{18}H_{16}OClSb$ Triphenylstibine hydroxychloride (MORGAN, MICKLETHWAIT, and WHITBY), T., 37.

$C_{18}H_{16}O_4NSb$ Triphenylstibine hydroxynitrate (MORGAN, MICKLETHWAIT and WHITBY), T., 35.

C_{19} Group.

$C_{19}H_{12}O_3$ 3-Hydroxy-9-phenylfluorone (POPE and HOWARD), T., 1026.

$C_{19}H_{14}O_3$ 3:6-Dihydroxy-9-phenylxanthen (POPE and HOWARD), T., 81.

$C_{19}H_{18}O_5$ Piperonylidene-4:5-dimethoxy-*o*-methylacetophenone (HARDING and WEIZMANN), T., 1128.

$C_{19}H_{20}O_6$ Matairesinol (+Et OH) (EASTERFIELD and BEE), T., 1028 ; P., 7.

$C_{19}H_{22}O_6$ Benzoyloxydiacetyldimethoxybenzene (TUTIN and CATON), T., 2066.

$C_{19}H_{22}O_7$ Matairesinolic acid (+ $3H_2O$), and its calcium salt (EASTERFIELD and BEE), T., 1031 ; P., 7.

$C_{19}H_{26}Si$ Dibenzylethylpropylsilicane (CHALLENGER and KIPPING), T., 146 ; P., 3.

$C_{19}H_{28}O_3$ Menthyl *o*-, *m*-, and *p*-ethoxybenzoate (COHEN and DUDLEY), T., 1741.

$C_{19}H_{30}N_2$ Menthylethylbenzamidine, and its salts (COHEN and MARSHALL), T., 333.

$C_{19}H_{32}O_{11}$ Methyl pentamethylgynocardinate (MOORE and TUTIN), T., 1287 ; P., 182.

$C_{19}H_{33}N$ Tridecylaniline, and its hydrochloride (LE SUEUR), T., 2440 ; P., 290.

$C_{19}H_{34}O_4$ Di*iso*amyl α-thujadicarboxylate (THOMSON), T., 1514 ; P., 178.

19 III

$C_{19}H_8O_3Br_4$ Tetrabromo-3-hydroxy-9-phenylfluorone (POPE and HOWARD), T., 82.

$C_{19}H_{12}O_6N_4$ Substance, from acridine and trinitrobenzene (SUDBOROUGH and BEARD), T., 796.

Substance, from α- and β-naphthaquinoline and trinitrobenzene (SUDBOROUGH and BEARD), T., 795.

$C_{19}H_{13}ON_3$ 5-α-Naphthaleneazo-8-hydroxyquinoline, and its hydrochloride and sodium salt (FOX), T., 1345.

Quinoline-3-azo-β-naphthol (MILLS and WATSON), T., 753 ; P., 56.

$C_{19}H_{13}O_2N_3$ *α-oo*-Tricyano-$\beta\beta'$-diphenyl*iso*butyric acid, and its potassium salt (MITCHELL and THORPE), T., 2280.

$C_{19}H_{14}O_8N_6$ Substance, from *m*-nitrobenzaldehydephenylhydrazone and trinitrobenzene (SUDBOROUGH and BEARD), T., 793.

$C_{19}H_{15}NS$ Diphenylthiobenzamide, preparation of (RUSSELL), T., 956.

$C_{19}H_{16}O_3N_2$ Benzoyl-4-nitroethyl-α-naphthylamine (MORGAN and COUZENS), T., 1693.

$C_{19}H_{16}O_6N_4$ Substance, from benzylaniline and trinitrobenzene (SUDBOROUGH and BEARD), T., 788.

$C_{19}H_{17}O_2N_3$ Nitrosamine, from hydrolysis of benzoylethyl-4-aminonaphthalene-1-diazonium salts (MORGAN and COUZENS), T., 1696.

$C_{19}H_{18}ON_2$ *as*-Benzoylethyl-1:4-naphthalenediamine (MORGAN and COUZENS), T., 1693 ; P., 165.

$C_{19}H_{18}O_3N_2$ *cyclo*Pentan-1-one-2:5-dicarbanilide (MITCHELL and THORPE), T., 1003.

$C_{19}H_{20}O_3N_4$ 1:7-Dibenzyltetrahydrouric acid (FRANKLAND), T., 1691 ; P., 203.

$C_{19}H_{20}O_{12}S_2$ Matairesinoldisulphonic acid, barium salt ($+5H_2O$) (EASTERFIELD and BEE), T., 1030 ; P., 7.

$C_{19}H_{21}O_3N$ Laureline, and its salts (ASTON), T., 1386 ; P., 11.

$C_{19}H_{22}O_2N_2$ Ethyl 3-anilino-1:1-dimethyl-Δ^3-*cyclo*hexenylidene-5-cyanoacetate (CROSSLEY and GILLING), T., 527.

$C_{19}H_{29}O_2N$ Menthyl *o*-, and *p*-dimethylaminobenzoate (COHEN and DUDLEY), T., 1746.

$C_{19}H_{32}ON_2$ Phenyltridecylnitrosoamine (LE SUEUR), T., 2440.

19 IV

$C_{19}H_{13}O_8N_3S$ Dinitro-*S*-salicylphenazothionium hydroxide (BARNETT and SMILES), T., 372.

$C_{19}H_{16}ON_3Cl$ Benzoylethyl-4-aminonaphthalene-1-diazonium chloride (MORGAN and COUZENS), T., 1695.

$C_{19}H_{16}O_5N_3Cl$ Benzoylethyl-4-aminonaphthalene-1-diazonium perchlorate (MORGAN and COUZENS), T., 1695.

$C_{19}H_{17}O_5N_3S$ Benzoylethyl-4-aminonaphthalene-1-diazonium sulphate ($+EtOH$) (MORGAN and COUZENS), T., 1694.

$C_{19}H_{26}O_3SSi$ *dl*-Dibenzylethylpropylsilicanesulphonic acid, metallic salts of (CHALLENGER and KIPPING), T., 152 ; alkaloidal salts of (CHALLENGER and KIPPING), T., 760.

l-Dibenzylethylpropylsilicanesulphonic acid, alkaloidal salts of (CHALLENGER and KIPPING), T., 760.

$C_{19}H_{26}O_6S_2Si$ Dibenzylethylpropylsilicanedisulphonic acid, metallic salts of (CHALLENGER and KIPPING), T., 153.

19 V

$C_{19}H_{17}ON_3Cl_6Sn$ Benzoylethyl-4-aminonaphthalene-1-diazonium stannichloride (MORGAN and COUZENS), T., 1695.

C_{20} Group.

$C_{20}H_{14}O_2$ 9-Phenyl-2-methylfluorone (POPE and HOWARD), T., 1026.

$C_{20}H_{16}O_2$ 6-Hydroxy-9-phenyl-2-methylxanthen (POPE and HOWARD), T., 81.

$C_{20}H_{16}O_4$ 3:6-Dihydroxy-4′-methoxy-9-phenylxanthen (POPE and HOWARD), T., 974.

$C_{20}H_{18}O_2$ *l*-*αβ*-Dihydroxy-*αββ*-triphenylethane (McKENZIE and WREN), T., 480.

$C_{20}H_{21}N$ 2-*tert.*-Butyl-4:5-diphenylpyrrole (BOON), T., 1260; P., 95.

$C_{20}H_{22}O_2$ Desylpinacoline (*α-tert.-butyryl-β-benzoylphenylethane*) (BOON), T., 1258.

$C_{20}H_{22}O_4$ *α*- and *β*-Naphthyl hydrogen camphorate (EDMINSON and HILDITCH), T., 227.

$C_{20}H_{22}O_6$ 2:4:6-Trimethoxyphenyl 3:4-dimethoxystyryl ketone (TUTIN and CATON), T., 2067; P., 223.

$C_{20}H_{24}O_5$ *o*-*β*-Acetylvinylphenyl hydrogen camphorate (EDMINSON and HILDITCH), T., 227.

$C_{20}H_{26}N_2$ Ethylidenexylidine, bimolecular (JONES and WHITE), T., 641; absorption spectrum of (PURVIS), T., 645.

$C_{20}H_{28}O_3$ Menthyl *o*-, and *p*-allyloxybenzoate (COHEN and DUDLEY), T., 1745.

$C_{20}H_{30}O_3$ Menthyl *o*-, *m*-, and *p*-propoxybenzoate (COHEN and DUDLEY), T., 1742.

Menthyl *o*- and *p*-*iso*propoxybenzoate (COHEN and DUDLEY), T., 1743.

$C_{20}H_{34}O$ Phytosterol, from colocynth (POWER and MOORE), T., 108.

20 III

$C_{20}H_{12}O_2S_2$ Dinaphthylene *p*-disulphoxide (HILDITCH), T., 2591.

$C_{20}H_{16}ON_2$ *iso*Phenylmethylacetyl*cyclo*pentenephenazine (RUHEMANN), T., 1444.

$C_{20}H_{16}ON_4$ Benzoylethyl-4-aminonaphthalene-1-diazonium cyanide (MORGAN and COUZENS), T., 1695.

$C_{20}H_{16}O_2N_2$ Salicylphenylbenzamidine (TITHERLEY), T., 209; P., 9.

$C_{20}H_{16}O_7N$ Anhydrocotarninenitrophthalide (HOPE and ROBINSON), P., 230.

$C_{20}H_{17}ON$ 8-Hydroxy-5-phenyl-3-methyldihydroacridine (POPE and HOWARD), T., 83.

$C_{20}H_{17}O_4N$ Berberine, constitution of (PERKIN and ROBINSON), T., 305; P., 24.

$C_{20}H_{17}O_6N_5$ Substance, from *oo*-diaminostilbene and trinitrobenzene (SUDBOROUGH and BEARD), T., 791.

$C_{20}H_{19}O_3S$ Substance, from 2:3-diketo-1-acetyl-4-phenyl-5-methyl*cyclo*pentene and phenylmercaptan (RUHEMANN), T., 1444.

$C_{20}H_{19}O_5N$ Anhydrocotarnineaminophthalide (HOPE and ROBINSON), P., 230.

$C_{20}H_{20}O_4N_2$ *mm'pp'*-Tetramethoxy-2:5-diphenylpyrazine, and its salts (TUTIN), T., 2510 ; P., 244 ; (TUTIN and CATON), T., 2533 ; P., 245.

mm'pp'-Tetramethoxy-2:6-diphenylpyrazine, and its salts (TUTIN), T., 2511 ; P., 244 ; (TUTIN and CATON), T., 2533 ; P., 245.

$C_{20}H_{21}O_2N$ α-, and β-Naphthylcamphorimide (WOOTTON), T., 415.

$C_{20}H_{21}O_4N$ Papaverine, constitution of the reduction products of (PYMAN and REYNOLDS), T., 1320 ; P., 180.

$C_{20}H_{22}O_4S$ α- and β-Naphthyl camphor-β-sulphonate (EDMINSON and HILDITCH), T., 228.

$C_{20}H_{23}O_2N$ Oxime of desylpinacoline (BOON), T., 1258.

$C_{20}H_{23}O_3N$ α- and β-Naphthyl α-camphoramic acid (WOOTTON), T., 415.

$C_{20}H_{23}O_4N$ Pavine, and its hydriodide (PYMAN and REYNOLDS), T., 1327 ; P., 180 ; preparation and resolution of (POPE and GIBSON), T., 2207 ; P., 250.

d- and *l*- Pavine, rotatory power of salts of, with *d*- tartaric acid and *d*- and *l*-camphor-β-sulphonic acid (POPE and GIBSON), T., 2211 ; P., 250.

$C_{20}H_{24}O_2N_2$ Ethyl 3-methylanilino-1:1-dimethyl-Δ^3-*cyclo*hexenylidene-5-cyanoacetate (CROSSLEY and GILLING), T., 527.

Dioxime of desylpinacoline (BOON), T., 1259.

$C_{20}H_{24}O_5S$ *o*-β-Acetylvinylphenyl camphor-β-sulphonate (EDMINSON and HILDITCH), T., 228.

$C_{20}H_{30}O_4S_2$ Dicamphoryl β-α-disulphoxide (HILDITCH), T., 1096 ; P., 95.

$C_{20}H_{31}O_4P$ Dicamphorylphosphinic acid, and its metallic salts (MORGAN and MOORE), T., 1697.

20 IV

$C_{20}H_{13}O_9N_5S$ Tetranitro-*S*-phenetylphenazothionium hydroxide, and its sulphate (BARNETT and SMILES), T., 368.

$C_{20}H_{14}ON_2Cl_2$ 4:4′-Dichlorobenzilphenylhydrazone (KENNER and WITHAM), T., 1967.

$C_{20}H_{34}O_4BrS$ *d*-Bornylamine *d*-α-bromocamphor-π-sulphonate (POPE and READ), T., 994.

20 V

$C_{20}H_{13}ONCl_4S$ Tetrachloro-*S*-phenetylphenazothionium hydroxide ($+H_2O,CHCl_3$) (BRADY and SMILES), T., 1561.

$C_{20}H_{28}O_4NBrS$ *d*-(*l*)-Tetrahydroquinaldine *d*-(*l*-)α-bromocamphor-π-sulphonate (POPE and READ), T., 2203.

C_{21} Group.

$C_{21}H_{14}O_4$ 3-Acetoxy-9-phenylfluorone (POPE and HOWARD), T., 1027.

$C_{21}H_{16}O_6$ Ethyl 2-keto-3-acetoxy-4:5-diphenylene-2:3-dihydrofuran-3-carboxylate (RICHARDS), T., 1457 ; P., 195.

$C_{21}H_{16}O_9$ Acetyl derivative of substance, from red clover flowers (POWER and SALWAY), T., 239.

$C_{21}H_{17}N$ 2:3-Diphenyl-1-methylindole, preparation of (RICHARDS), T., 978.

$C_{21}H_{18}O_3$ 6-Hydroxy-4′-methoxy-9-phenyl-2-methylxanthen (POPE and HOWARD), T., 974.

$C_{21}H_{20}O_2$ *i*-α-Methoxy-αββ-triphenylethane (MCKENZIE and WREN), T., 483.

l-α-Methoxy-αββ-triphenylethane (MCKENZIE and WREN), T., 485.

$C_{21}H_{20}O_{11}$ Quercitrin, and its trisodium derivative (MOORE), P., 182.

$C_{21}H_{20}O_{12}$ Serotrin ($+3H_2O$) (POWER and MOORE), T., 1109 ; P., 124.

Incarnatrin, from clover flowers (ROGERSON), T., 1008 ; P., 112.

$C_{21}H_{22}O_7$ Acetylmatairesinol (EASTERFIELD and BEE), T., 1030 ; P., 7.

$C_{21}H_{34}N_2$ Menthyldiethylbenzamidine, and its salts (COHEN and MARSHALL), T., 333.

$C_{21}H_{36}O_4$ Trifolianol (Power and Salway), T., 249 ; P., 20.

$C_{21}H_{37}N$ Pentadecylaniline, and its hydrochloride (Le Sueur), T., 2438 ; P., 290.

21 III

$C_{21}H_{13}O_4Cl$ 1 (or 4)-Chloro-8-hydroxy-4 (or 1)-phenoxy-5-methylanthraquinone (Walsh and Weizmann), T., 690.

$C_{21}H_{16}ON_4$ Diphenylhydrazone of triketohydrindene (Ruhemann), T., 1448.

$C_{21}H_{17}O_2N_3$ Ethyl *α-oo*-tricyano-*ββ'*-diphenyl*iso*butyrate (Mitchell and Thorpe), T., 2280.

$C_{21}H_{19}O_2N$ 8-Hydroxy-5-*p*-methoxyphenyl-3-methyldihydroacridine (Pope and Howard), T., 975.

$C_{21}H_{22}O_2N_2$ Strychnine, constitution of (Perkin and Robinson), T., 305 ; P., 24.

Substance, from piperidine and diketodiphenylpyrroline (Ruhemann), T., 465.

$C_{21}H_{25}O_4N$ *N*-Methylpavine, and its salts (Pyman and Reynolds), T., 1324 ; P., 180.

$C_{21}H_{27}O_4N$ Laudanosine hydrogen oxalate (+1½ or 2½H_2O) (Pyman and Reynolds), T., 1323.

$C_{21}H_{35}ON$ Acetotridecylaniline (Le Sueur), T., 2440.

$C_{21}H_{36}ON_2$ Phenylpentadecylnitrosoamine (Le Sueur), T., 2439.

21 IV

$C_{21}H_{17}O_4N_3S$ Dinitro-*S*-mesitylphenazothionium hydroxide (+H_2O) (Barnett and Smiles), T., 371.

$C_{21}H_{18}O_6N_4S$ Phenetoleazosulphobenzylidene-*p*-nitroaniline, potassium salt (Green and Sen), T., 2245.

$C_{21}H_{19}O_4N_3S$ Phenetoleazosulphobenzylideneaniline (Green and Sen), T., 2244.

$C_{21}H_{19}O_5N_3S$ Phenetoleazosulphobenzylidene-*p*-aminophenol, potassium salt (Green and Sen), T., 2245.

$C_{21}H_{19}O_7N_3S_2$ Phenetoleazosulphobenzylideneaniline-*p*-sulphonic acid, potassium salt (Green and Sen), T., 2244.

$C_{21}H_{25}O_4N_2Cl$ 6(or 7)-Methoxy-7(or 6)-[6:7-dihydroxy-2-methyl-3:4-dihydro*iso*quinoliniumoxy]-2-methyl-3:4-dihydro*iso*quinolinium chloride (Pyman), T., 279.

$C_{21}H_{25}O_4N_2I$ 6(or 7)-Methoxy-7(or 6)-[6:7-dihydroxy-2-methyl-3:4-dihydro*iso*quinoliniumoxy]-2-methyl-3:4-dihydro*iso*quinolinium iodide (Pyman), T., 279.

C_{22} Group.

$C_{22}H_{14}$ *αβα'β'*-Dinaphthanthracene, preparation of (Homer), T., 1141 ; P., 12 ; absorption spectra of, and of its hydro-derivative and isomerides (Homer and Purvis), T., 1155 ; P., 25.

22 II

$C_{22}H_{15}N_3$ Diphenylpyrrolinophenazine (Ruhemann), T., 1443 ; P., 196.

$C_{22}H_{18}O$ Phenylethylidenedeoxybenzoin (Ruhemann), T., 459.

$C_{22}H_{18}O_2$ Triphenylbutyrolactone (Purdie and Arup), T., 1543 ; P., 199.

$C_{22}H_{18}O_5$ Substance, from ethyl acetoacetate and phenanthraquinone (Richards), T., 1460 ; P., 195.

$C_{22}H_{19}N$ 2:3-Diphenyl-1-ethylindole (Richards), T., 978.

$C_{22}H_{20}O_6$ Ethyl 9-phenanthroxylacetoxyacetoacetate (Richards), T., 1459 ; P., 195.

$C_{22}H_{22}O_{11}$ Trifolin ($+H_2O$) (Power and Salway), T., 239 ; P., 20.
*iso*Trifolin (Power and Salway), T., 244 ; P., 20.
$C_{22}H_{24}O_2$ Diphenylcampholide (Shibata), T., 1240.
Lactone of diphenylhydroxycampholic acid (Shibata), T., 1241.
$C_{22}H_{24}O_5$ 2-Aceto-α-naphthyl hydrogen camphorate (Edminson and Hilditch), T., 228.
$C_{22}H_{26}O_3$ Diphenylhydroxycampholic acid, barium salt of (Shibata), T., 1240.
Diphenylhydroxy*iso*campholic acid (Shibata), T., 1246.
$C_{22}H_{28}O_3$ Menthyl α- and β-methoxynaphthoate (Cohen and Dudley), T., 1747.
$C_{22}H_{34}O_3$ Menthyl *o*-, *m*-, and *p*-*iso*amyloxybenzoate (Cohen and Dudley), T., 1744.
$C_{22}H_{38}O_4$ Citrullol, from colocynth (Power and Moore), T., 102 ; P., 3.

22 III

$C_{22}H_{14}O_{10}N_8$ 4:4′:7:7′-Tetranitro-6:6′-dihydroxy-1:1′-*p*-phenylene-2:2′-dimethylbisbenziminazole (Meldola and Kuntzen), P., 340.
$C_{22}H_{15}O_4N$ Substance, from ω-amino-*op*-dihydroxyacetophenone (Tutin), T., 2515.
$C_{22}H_{16}O_6N_4$ Substance, from trinitrobenzene and phenyl-β-naphthylamine (Sudborough and Beard), T., 789.
$C_{22}H_{16}O_6N_6$ Substance, from 1-benzeneazo-2-naphthylamine and trinitrobenzene (Sudborough and Beard), T., 787.
$C_{22}H_{22}O_6N_2$ Dinitrodiphenylcampholide (Shibata), T., 1241.
$C_{22}H_{22}O_9N$ Nitrognoscopine, and its salts (Hope and Robinson), P., 229.
$C_{22}H_{23}O_7N$ Gnoscopine (*dl-narcotine*), synthesis of (Perkin and Robinson), P., 46 ; resolution of (Perkin and Robinson), P., 131.
d- and *l*-Narcotine, *d*-bromocamphorsulphonates of (Perkin and Robinson), P., 131.
$C_{22}H_{24}O_5S$ 2-Aceto-α-naphthyl camphor-β-sulphonate (Edminson and Hilditch), T., 228.
$C_{22}H_{24}O_7N$ Aminognoscopine (Hope and Robinson), P., 230.
$C_{22}H_{28}O_4N_2$ αθ-Dianilinosebacic acid, and its silver salt (Le Sueur and Haas), T., 180.

22 IV

$C_{22}H_{17}O_2NS$ Substance, from phenylmercaptan and diketodiphenylpyrroline (Ruhemann), T., 464.
$C_{22}H_{19}O_7N_3S$ Phenetoleazosulphobenzylideneaminosalicylic acid, potassium salt (Green and Sen), T., 2245.
$C_{22}H_{24}O_4N_4S$ Phenetoleazosulphobenzylidene-*p*-phenylenedimethyldiamine, potassium salt (Green and Sen), T., 2245.
$C_{22}H_{27}O_4N_2Cl$ 6 (or 7)-Methoxy-7 (or 6)-[7 (or 6)-hydroxy-6 (or 7)-methoxy-2-methyl-3:4-dihydro*iso*quinoliniumoxy]-2-methyl-3:4-dihydro*iso*quinolinium chloride (Pyman), T., 278.

C_{23} Group.

$C_{23}H_{16}O_2$ 4:5:6-Triphenyl-2-pyrone (Ruhemann), T., 459 ; P., 59.
8-Hydroxy-11-phenyl-β-naphthaxanthen (Pope and Howard), T., 82.
$C_{23}H_{17}N_3$ Phenyl-*p*-tolylpyrrolinophenazine (Ruhemann), T., 1444.
$C_{23}H_{18}O_8$ Triacetylpratensol (Power and Salway), T., 238.
$C_{23}H_{20}O_4$ 6-Acetoxy-4′-methoxy-9-phenyl-2-methylxanthen (Pope and Howard), T., 974.

$C_{23}H_{22}O_7$ Ethyl phenanthroxylacetoxymalonate (Richards), T., 1457; P., 195.

$C_{23}H_{28}O_3$ Methyl diphenylhydroxy*iso*campholate (Shibata), T., 1245.

$C_{23}H_{30}N_2$ Phenylmenthylbenzamidine, and its hydrochloride and platinichloride (Cohen and Marshall), T., 330.

$C_{23}H_{41}N$ Heptadecylaniline, and its hydrochloride (Le Sueur), T., 2435; P., 290.

23 III

$C_{23}H_{16}O_6N_4$ Substance, from benzylidene-α-naphthylamine and trinitrobenzene (Sudborough and Beard), T., 793.

Substance, from αα-diphenylpyridine and trinitrobenzene (Sudborough and Beard), T., 794.

$C_{23}H_{17}ON$ 10-Hydroxy-7-phenyldihydro-αβ-phenonaphthacridine (Pope and Howard), T., 976.

$C_{23}H_{17}O_5Cl$ 3:6-Diacetoxy-9-phenylxanthonium chloride (Pope and Howard), T., 1027.

$C_{22}H_{18}O_3N_2$ 3-Benzoylamino-3-hydroxy-2-keto-4:5-diphenylpyrroline, decomposition of (Ruhemann), T., 463.

$C_{23}H_{18}O_6N_4$ Substance, from α- and β-naphthylamine and trinitrobenzene (Sudborough and Beard), T., 788.

$C_{23}H_{21}O_3N$ Dibenzoyl derivative of *p*-hydroxyphenylethylmethylamine (Walpole),, T., 946.

8-Acetoxy-5-*p*-methoxyphenyl-3-methyldihydroacridine (Pope and Howard), T., 975.

$C_{23}H_{23}O_7N_5$ Substance, from tetramethyldiaminobenzophenone and trinitrobenzene (Sudborough and Beard), T., 792.

$C_{23}H_{25}O_6N_5$ Substance, from tetramethyl-*p*-diaminodiphenylmethane and trinitrobenzene (Sudborough and Beard), T., 791.

$C_{23}H_{25}O_7N_5$ Substance, from tetramethyldiaminobenzhydrol and trinitrobenzene (Sudborough and Beard), T., 792.

$C_{23}H_{26}O_{10}N_2$ Nitronarceine (Hope and Robinson), P., 230.

$C_{23}H_{39}ON$ Acetopentadecylanilide (Le Sueur), T., 2439.

$C_{23}H_{40}ON_2$ Phenylheptadecylnitrosoamine (Le Sueur), T., 2437.

23 IV

$C_{23}H_{19}O_3N_3S$ Toluene-ω-sulphonyl-*p*-aminobenzeneazo-β-naphthol (Morgan and Pickard), T., 57.

$C_{23}H_{23}O_6N_5S$ Substance, from tetramethyldiaminothiobenzophenone and trinitrobenzene (Sudborough and Beard), T., 792.

C_{24} Group.

$C_{24}H_{16}O_3$ Benzoyl derivative of 2-benzo-α-naphthol (Edminson and Hilditch), T., 226.

$C_{24}H_{18}O_3$ 8-Hydroxy-11-*p*-methoxyphenyl-β-naphthaxanthen (Pope and Howard), T., 975.

$C_{24}H_{18}O_{10}$ Acetyl derivative of trifolitin (Power and Salway), T., 240.

$C_{24}H_{18}O_{11}$ Acetyl derivative of substance, from red clover flowers (Power and Salway), T., 286.

$C_{24}H_{20}O_6$ 3:6-Diacetoxy-4′-methoxy-9-phenylxanthen (Pope and Howard), T., 974.

$C_{24}H_{22}O_{10}$ Tetra-acetylhesperitin (Tutin), T., 2061.

$C_{24}H_{30}O_3$ Menthyl *o*-, and *p*-benzyloxybenzoate (Cohen and Dudley) T., 1745.

$C_{24}H_{30}O_5$ Elaterone (Moore), T., 1803; P., 215.

$C_{24}H_{32}O_4$ Substance, from oxidation of elateric acid (Moore), T., 1804; P., 215.

$C_{24}H_{32}N_2$ *o*-, *m*-, and *p*-Tolylmenthylbenzamidine, and their hydrochlorides and platinichlorides (Cohen and Marshall), T., 331.

$C_{24}H_{40}O_2$ Starch, iodine reaction for (Harrison), P., 252.

24 III

$C_{24}H_{12}O_2S_2$ Naphthabisthioxanthone (Davis and Smiles), T., 1298; P., 174.

$C_{24}H_{18}O_7N_4$ Acetyl derivative of substance, from phenyl-β-naphthylamine and trinitrobenzene (Sudborough and Beard), T., 789.

$C_{24}H_{19}O_2N$ 10-Hydroxy-7-*p*-methoxyphenyldihydro-αβ-phenonaphthacridine (Pope and Howard), T., 976; P., 88.

$C_{24}H_{20}O_6N_4$ Substance, from benzyl-β-naphthylamine and trinitrotoluene (Sudborough and Beard), T., 788.

$C_{24}H_{25}O_6N_6$ Substance, from diethylaminobenzylidene-*p*-aminomethylaniline and trinitrobenzene (Sudborough and Beard), T., 791.

$C_{24}H_{26}O_8N$ Acetylaminognoscopine (Hope and Robinson), P., 230.

$C_{24}H_{32}O_4N_2$ Methyl αθ-dianilinosebacate (Le Sueur and Haas), T., 180.

$C_{24}H_{32}O_5N_2$ Dioxime of elaterone (Moore), T., 1804.

24 IV

$C_{24}H_{15}O_6N_9S_3$ Benzene-1:3:5-trisulphonylter-*p*-phenylenediazoimide (Morgan and Pickard), T., 54.

$C_{24}H_{18}O_{12}N_6S_3$ Benzene-1:3:5-trisulphonylter-*m*- and *p*-nitroaniline (Morgan and Pickard), T., 54.

$C_{24}H_{18}N_8Cl_6Pt$ Benzeneazobenzenediazonium platinichloride (Hewitt and Thole), T., 515; P., 54.

$C_{24}H_{24}O_6N_6S_3$ Benzene-1:3:5-trisulphonylter-*p*-phenylenediamine (Morgan and Pickard), T., 55.

C_{25} Group.

$C_{25}H_{24}O_{12}$ Carthamine, and its potassium salt (Kametaka and Perkin), T., 1415; P., 181.

Xanthocarthanimic acid, salts of (Kametaka and Perkin), T., 1425; P., 181.

$C_{25}H_{26}O_5$ *o*-β-Benzoylvinylphenyl hydrogen camphorate (Edminson and Hilditch), T., 227.

$C_{25}H_{34}N_2$ Phenylmenthylethylbenzamidine, and its salts (Cohen and Marshall), T., 331.

$C_{25}H_{40}O_6$ Acetyl derivative of trifolianol (Power and Salway), T., 249.

25 III

$C_{25}H_{17}O_{12}N_7$ Substance, from benzylideneaniline and trinitrobenzene (Sudborough and Beard), T., 793.

$C_{25}H_{18}O_{12}N_8$ Substance, from benzaldehydephenylhydrazone and trinitrobenzene (Sudborough and Beard), T., 793.

$C_{25}H_{19}O_2N$ Acetyl derivative of 10-hydroxy-7-phenyldihydro-αβ-phenonaphthacridine) (Pope and Howard), T., 977.

$C_{25}H_{26}O_2N_4$ Hydrate of 2:3-bis-(*p*-dimethylaminoanilo)-α-hydrindone (Ruhemann), T., 1445; P., 196.

$C_{25}H_{26}O_5S$ *o*-β-Benzoylvinylphenyl camphor-β-sulphonate (Edminson and Hilditch), T., 228.

$C_{25}H_{27}O_3N_9$ Substance, from the action of *p*-triazobenzaldehyde on camphoryl-ψ-semicarbazide (Forster and Judd), T., 261.

$C_{25}H_{43}ON$ Acetoheptadecylanilide (Le Sueur), T., 2437.

25 IV

$C_{25}H_{21}O_4N_3S$ Phenetoleazosulphobenzylidene-*α*- and *β*-naphthylamine, potassium salts (GREEN and SEN), T., 2246.

$C_{25}H_{33}O_7NS$ Benzoyloscine *d*-camphorsulphonate (TUTIN), T., 1795; P. 215.

25 V

$C_{25}H_{32}O_7NBrS$ Benzoyl-*d*-oscine *d*-bromocamphorsulphonate (TUTIN), T., 1798; P., 215.

C_{26} Group.

$C_{26}H_{16}O_4$ 1:4-Diphenoxyanthraquinone (WALSH and WEIZMANN), T., 688.

$C_{26}N_{18}O_2$ *α*-*γ*-Diphenyl-*γ*-1-naphthylallene-*α*-carboxylic acid (LAPWORTH and WECHSLER), T., 45.

Substance, from diphenylnaphthylallenecarboxylic acid and acetic acid (LAPWORTH and WECHSLER), T., 47.

$C_{26}H_{19}N$ 1:2:3-Triphenylindole (RICHARDS), T., 978.

$C_{26}H_{20}O_2$ *αγ*-Diphenyl-*γ*-1-naphthylbutyrolactone (LAPWORTH and WECHSLER), T., 42.

$C_{26}H_{20}O_4$ 8-Acetoxy-11-*p*-methoxyphenyl-*β*-naphthaxanthen (POPE and HOWARD), T., 975.

$C_{26}H_{25}N$ 1:4:5-Triphenyl-2-*tert.*-butylpyrrole (BOON), T., 1260.

$C_{26}H_{28}N_2$ 1-Anilino-2-*tert.*-butyl-4:5-diphenylpyrrole (BOON), T., 1259; P., 94.

1:3:4-Triphenyl-6-*tert.*-butyldihydropyridazine (BOON), T., 1259; P., 94,

$C_{26}H_{42}O_6$ Diacetylcitrullol (POWER and MOORE), T., 102.

26 III

$C_{26}H_{14}O_8N_2$ Dinitro-1:4-diphenoxyanthraquinone (WALSH and WEIZMANN), T., 689.

$C_{26}H_{17}O_2Br$ Bromolactone from ethyl *αγ*-diphenyl-*γ*-1-naphthylallene-*α*-carboxylate (LAPWORTH and WECHSLER), T., 47.

$C_{26}H_{20}O_{12}N_8$ Substance, from acetophenonephenylhydrazone and trinitrobenzene (SUDBOROUGH and BEARD), T., 794.

$C_{26}H_{21}O_3N$ 10-Acetoxy-7-*p*-methoxyphenyldihydro-*αβ*-phenonaphthacridine (POPE and HOWARD), T., 976.

$C_{26}H_{22}O_{12}N_{10}$ Substance, from *p*-aminobenzeneazodimethylaniline (SUDBOROUGH and BEARD), T., 787.

$C_{26}H_{36}O_4N_2$ Ethyl *αθ*-dianilinosebacate (LE SUEUR and HAAS), T., 180.

C_{27} Group.

$C_{27}H_{20}O_5$ 2:4-Dibenzoyloxybenzhydrol (POPE and HOWARD), T., 80.

$C_{27}H_{22}O$ Tetraphenylacetone (SMEDLEY), T., 1491; P., 149.

$C_{27}H_{28}O_5$ 2-Benzo-*α*-naphthyl hydrogen camphorate (EDMINSON and HILDITCH), T., 228.

$C_{27}H_{30}O_{16}$ Rutin (+3H_2O), occurrence of, in *Tephrosia purpurea* (CLARKE and BANERJEE), T., 1837; P., 213.

Osyritrin (*violaquercitrin*), occurrence of, in *Osyris abyssinica* (AULD), P., 146.

Osyritrin, myrticolorin, violaquercitrin and rutin (+3H_2O), identity of (PERKIN), T., 1776; P., 213.

$C_{27}H_{40}N_2$ *d*-Borny ornylbenzamidine, and its salts (COHEN and MARSHALL), T., 334.

$C_{27}H_{46}O$ Verosterol ($+H_2O$) (Power and Rogerson), T., 1951; P., 219.

Phytosterol, from colocynth (Power and Moore), T., 105.

Phytosterol, from gelsemium (Moore), T., 2226; P., 247.

Phytosterol, (and $+H_2O$) from *Trifolium incarnatrin* (Rogerson), T. 1012; P., 112.

27 III

$C_{27}H_{20}O_{12}N_8$ Substance, from cinnamaldehydephenylhydrazone and trinitrobenzene (Sudborough and Beard), T., 793.

$C_{27}H_{21}O_2N$ 8-Benzoyloxy-5-phenyl-3-methyldihydroacridine (Pope and Howard), T., 83.

$C_{27}H_{35}O_5N_3$ Quinine 4-oximino*cyclo*hexanecarboxylate ($+2\frac{1}{2}H_2O$) (Mills and Bain), T., 1872.

27 IV

$C_{27}H_{23}O_4N_5S$ Phenetoleazosulphobenzylideneaminoazobenzene, potassium salt (Green and Sen), T., 2246.

C_{28} Group.

$C_{28}H_{22}O$ 2:2:5:5-Tetraphenyl-2:5-dihydrofuran (Purdie and Arup), T. 1542; P., 199.

$C_{28}H_{22}O_2$ Ethyl $\alpha\gamma$-diphenyl-γ-1-naphthylallene-α-carboxylate (Lapworth and Wechsler), T., 44.

$C_{28}H_{22}O_6$ Dibenzoyl derivative of 2:4-dihydroxy-4′-methoxybenzhydrol (Pope and Howard), T., 973.

$C_{28}H_{32}O_3$ Menthyl β-benzoyloxynaphthoate (Cohen and Dudley), T., 1748.

$C_{28}H_{38}O_7$ α-Elaterin, constitution of (Moore), T., 1797; P., 215.

28 III

$C_{28}H_{19}O_{12}N_7$ Substance, from phenyl α- and β-naphthylamines and trinitrobenzene (Sudborough and Beard), T., 789.

$C_{28}H_{21}O_3N$ 2-Keto-3:3-bishydroxyphenyl-4:5-diphenylpyrroline (Ruhemann), T., 465.

$C_{28}H_{22}O_5S$ Dibenzoyl-*p*-cresol sulphoxide (Gazdar and Smiles), T., 2249.

C_{29} Group.

$C_{29}H_{44}N_2$ *d*-Bornyl-*l*-bornylethylbenzamidine, and its salts (Cohen and Marshall), T., 335.

29 III

$C_{29}H_{19}O_{12}N_7$ Substance, from benzylidene-β-naphthylamine and trinitrobenzene (Sudborough and Beard), T., 793.

$C_{29}H_{21}O_6N$ ω-Benzoylamino-*op*-dibenzoyloxyacetophenone (Tutin), T., 2515.

$C_{29}H_{21}O_{12}N_7$ Substance, from *p*-tolyl-α-naphthylamine and trinitrobenzene (Sudborough and Beard), T., 790.

Substance, from *o*- and *p*-tolyl-β-naphthylamines and trinitrobenzene (Sudborough and Beard), T., 790.

$C_{29}H_{26}O_{13}N_8$ Substance, from tetramethyldiaminobenzophenone and trinitrobenzene (Sudborough and Beard), T., 792.

$C_{29}H_{29}O_6N_5$ Substance, from tetramethyldiaminotriphenylmethane and trinitrobenzene (Sudborough and Beard), T., 792.

29 V

$C_{29}H_{25}O_3NSSi$ β-Naphthylamine *l*-dibenzylethylpropylsilicanesulphonate (CHALLENGER and KIPPING), T., 770.

$C_{29}H_{47}O_3NSSi$ *l*-Menthylamine *dl*-dibenzylethylpropylsilicanesulphonate (+2H_2O) (CHALLENGER and KIPPING), T., 152.

C_{30} Group.

$C_{30}H_{20}O_3$ 8-Benzoyloxy-11-phenyl-β-naphthaxanthen (POPE and HOWARD), T., 83.

$C_{30}H_{21}N$ 1:2:3-Triphenyl-*a* and β-naphthindoles (RICHARDS), T., 979.

$C_{30}H_{28}O_3$ 3:4-Dimethoxy-2:2:5:5-tetraphenyltetrahydrofuran (PURDIE and YOUNG), T., 1535 ; P., 198.

30 III

$C_{30}H_{20}O_4N_2$ *oo'*-Dibenzoyloxy-2:5-diphenylpyrazine (TUTIN), T., 2519.

$C_{30}H_{23}O_{12}N_7$ Substance, from phenyl-*a*-naphthylamine and trinitrotoluene (SUDBOROUGH and BEARD), T., 789.

$C_{30}H_{24}O_6N_4$ Substance, from dibenzyl-β-naphthylamine and trinitrobenzene (SUDBOROUGH and BEARD), T., 791.

$C_{30}H_{29}O_{15}N_5$ Narcotine salt of 2:3:5-trinitro-4-acetylaminophenol (MELDOLA and KUNTZEN), T., 452.

$C_{30}H_{36}O_4N_2$ Elateronephenylhydrazone (MOORE), T., 1803.

30 IV

$C_{30}H_{28}O_8N_6S_2$ Bisphenetoleazobenzaldazinedisulphonic acid, potassium salt (GREEN and SEN), T., 2247.

$C_{30}H_{39}O_8NS$ *d*- and *l*-Pavine camphor-β-sulphonate (POPE and GIBSON), T., 2211.

d-Pavine *l*-camphor-β-sulphonate and *l*-pavine *d*-camphor-β-sulphonate (POPE and GIBSON), T., 2212.

$C_{30}H_{45}O_3Cl_2Sb$ Tricamphorylstibine chloride (MORGAN, MICKLETHWAIT, and WHITBY), T., 85.

30 V

$C_{30}H_{38}O_8NBrS$ *d*-Pavine *l*-*a*-bromocamphor-π-sulphonate (POPE and GIBSON), T., 2209.

C_{31} Group.

$C_{31}H_{50}O_3$ Prunol (+H_2O), and its sodium salt (POWER and MOORE), T., 1104 ; P., 124.

31 III

$C_{31}H_{26}O_6N_4$ Substance, from dibenzyl-β-naphthylamine and trinitrotoluene (SUDBOROUGH and BEARD), T., 791.

$C_{31}H_{31}O_{12}N$ Aniline xanthocarthaminate (KAMETAKA and PERKIN), T., 1424 ; P., 182.

$C_{31}H_{32}O_{12}N_6$ Brucine salt of 2:3:5-trinitro-4-acetylaminophenol (MELDOLA and KUNTZEN), T., 451.

31 IV

$C_{31}H_{38}O_6N_2S$ Strychnine *d*- and *l*-camphor-π-sulphonate (+ H_2O) (POPE and READ), T., 990.

C_{32} Group.

$C_{32}H_{52}O_3$ Methylprunol ($+ H_2O$) (Power and Moore), T., 1106.

32 III

$C_{32}H_{21}O_{12}N_7$ Substance, from αα-, and ββ-dinaphthylamine and trinitrobenzene (Sudborough and Beard), T., 789.

C_{33} Group.

$C_{33}H_{22}O_5$ 3:6-Dibenzoyloxy-9-phenylxanthen (Pope and Howard), T., 82.
$C_{33}H_{28}O_8$ Dibenzoylmatairesinol (Easterfield and Bee), T., 1030.
$C_{33}H_{52}O_8$ Acetylprunol (Power and Moore), T., 1105.

33 III

$C_{33}H_{36}O_7N_2$ Brucine salt of β-phenyl-β-methylglycidic acid (Wootton), T., 409; P., 44.

33 IV

$C_{33}H_{26}O_6N_6S_2$ Methanedisulphonylbis-*p*-aminobenzeneazo-β-naphthol (Morgan, Pickard, and Micklethwait), T., 60.

C_{34} Group.

$C_{34}H_{54}O_4$ Acetylmethylprunol (Power and Moore), T., 1106.
$C_{34}H_{70}O$ Incarnatyl alcohol (Rogerson), T., 1011; P., 112.

34 III

$C_{34}H_{38}O_4N_2$ Substance, from *p*-nitrobenzaldehyde and sodium camphor (Wootton), T., 411.

C_{35} Group.

$C_{35}H_{54}O_5$ Diacetylprunol (Power and Moore), T., 1105; P., 124.

35 III

$C_{35}H_{33}O_{12}N$ β-Naphthylamine xanthocarthaminate (Kametaka and Perkin), T., 1425; P., 182.

$C_{35}H_{41}O_6N_5$ Ergotoxine, and its salts (Barger and Ewins), T., 284; P., 2.

C_{36} Group.

$C_{36}H_{32}O_6SSb_2$ Triphenylstibine hydroxysulphate (Morgan, Micklethwait, and Whitby), T., 35.

$C_{36}H_{32}O_8N_6S_2$ Bisphenetoleazosulphobenzylidene-*p*-phenylenediamine, potassium salt (Green and Sen), T., 2247.

$C_{36}H_{47}O_6N_4Cl_3$ Trichlorobutylidenebis-3-aminophenyl-α-camphoramic acid (Wootton), T., 410.

36 V

$C_{36}H_{45}O_6NSSi$ Morphine *dl*- and *l*-dibenzylethylpropylsilicanesulphonate (Challenger and Kipping), T., 762.

C_{37} Group.

$C_{37}H_{36}O_{20}$ Octa-acetylserotrin (Power and Moore), T., 1109.

37 III

$C_{37}H_{45}O_6N_5$ Ergotoxine ethyl ester, phosphate and hydrochloride of (BARGER and EWINS), T., 286; P., 2.

C_{38} Group.

$C_{38}H_{33}O_2N_5$ Diazoamine, from ammonia and benzoylethyl-1:4-naphthylenediamine diazonium salts (MORGAN and COUZENS), T., 1696.

38 V

$C_{38}H_{48}O_4N_2SSi$ Cinchonidine *dl*- and *l*-dibenzylethylpropylsilicanesulphonate (CHALLENGER and KIPPING), T., 760.

C_{39} Group.

$C_{39}H_{50}O_5N_2SSi$ Quinine *dl* and *l*-dibenzylethylpropylsilicanesulphonate (CHALLENGER and KIPPING), T., 760.

$C_{39}H_{68}O_6N_2S_2Si$ *l*-Menthylamine dibenzylethylpropylsilicanedisulphonate (CHALLENGER and KIPPING), T., 153.

C_{40} Group.

$C_{40}H_{48}O_5N_2SSi$ Strychnine *dl*-dibenzylethylpropylsilicanesulphonate (and + $3H_2O$) (CHALLENGER and KIPPING), T., 150.

Strychnine *l*-dibenzylethylpropylsilicanesulphonate (CHALLENGER and KIPPING), T., 770.

C_{42} Group.

$C_{42}H_{74}O_4$ Incarnatyl hydrogen phthalate, sodium salt of (ROGERSON), T., 1011.

42 IV

$C_{42}H_{36}O_8N_6S_2$ Bisphenetoleazosulphobenzylidenebenzidine, potassium salt (GREEN and SEN), T., 2247.

42 V

$C_{42}H_{52}O_7N_2SSi$ Brucine *dl*-, *d*- and *l*-dibenzylethylpropylsilicanesulphonate (CHALLENGER and KIPPING), T., 766.

C_{44} Group.

$C_{44}H_{28}O_8N_2$ *oo'pp'*-Tetrabenzoyloxy-2:5-diphenylpyrazine (TUTIN), T., 2515.

$C_{44}H_{64}O_{20}N_2$ *d*- and *l*-Pavine *d*-tartrates (POPE and GIBSON), T., 2217.

C_{54} Group.

$C_{54}H_{30}O_9N_9S_3$ Benzene-1:3:5-trisulphonyltri-*p*-aminobenzeneazo-*β*-naphthol (MORGAN and PICKARD), T., 56.

C_{60} Group.

$C_{60}H_{76}O_{16}N_2Br_2S_2$ *dl*-Pavine *dl*-*α*-bromo-camphor-*π*-sulphonate (+ H_2O) (Pope and Gibson), T., 2210.

C_{61} Group.

$C_{61}H_{70}O_{10}N_4S_2Si$ Strychnine dibenzylethylpropylsilicanedisulphonate (Challenger and Kipping), T., 151.

C_{67} Group.

$C_{67}H_{48}O_{18}$ Benzoylcarthamine (Kametaka and Perkin), T., 1421; P., 181.

ERRATA.

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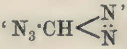
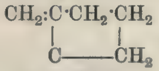
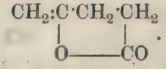
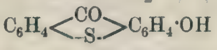
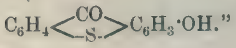
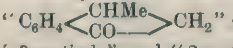
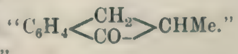
Page	Line	
55	19	*for* "$C_{24}H_{24}O_4N_4S_3$" *read* "$C_{24}H_{24}O_6N_6S_3$."
56	10	,, "$C_{54}H_{48}O_9N_9S_3$" *read* "$C_{54}H_{39}O_9N_9S_3$."
60	13*	,, "$C_{13}H_{26}O_6N_6S_2$" *read* "$C_{33}H_{26}O_6N_6S_2$."
82	1	,, "3:6-*Dibenzoyl*-9-*phenylxanthen*" read "3:6-*Dibenzoyloxy*-9-*phenylxanthen*."
464	2*	,, "$C_{22}H_{27}O_2NS$" *read* "$C_{22}H_{17}O_2NS$."
690	12	,, "$C_{15}H_8O_5Cl_2$" *read* "$C_{15}H_8O_3Cl_2$."
1032	16, 6*	*for* "2-Methyl-1:3-benzoxazine-4-one" *read* "2-Methyl-1:3-dihydrobenzoxazine-4-one."
1033	4, 11, 8*, 15*	
1056	10* *alter* formula to	" $N_3{\cdot}CH{<}\begin{array}{c}N\\ \ddot{N}\end{array}$"
1219 1221 1223 1225		in head-line *for* "NITROGEN" *read* "HYDROGEN."
1245	5	*for*  $\begin{array}{l}CH_2{:}C{\cdot}CH_2{\cdot}CH_2\\ \quad\vert\qquad\quad\vert\\ \;C\text{———}CH_2\end{array}$ *read*  $\begin{array}{l}CH_2{:}C{\cdot}CH_2{\cdot}CH_2\\ \quad\vert\qquad\quad\vert\\ \;O\text{———}CO\end{array}$.
1297	13*	,, " $C_6H_4{<}\begin{array}{c}CO\\ S\end{array}{>}C_6H_4{\cdot}OH$" *read* " $C_6H_4{<}\begin{array}{c}CO\\ S\end{array}{>}C_6H_3{\cdot}OH$."
1398	4*	,, "8-*Nitro*-6:7-*dimethylcoumarin*" read "5-*Nitro*-6:7-*dimethylcoumarin*."
1733	20	,, "270·8°" *read* "240·8°."
1738	11*	,, "Benzoylnaphthoyl" *read* "Benzoyl."
1826	2*	,, "deep orange" *read* "pale yellow."
2001	25	,, "has" *read* "have."
2274	16*	,, "3-*Methyl*-" read "2-*Methyl*."
2274	15*	,, " $C_6H_4{<}\begin{array}{c}CHMe\\ CO\end{array}{>}CH{\cdot}CO_2Et$" *read* " $C_6H_4{<}\begin{array}{c}CH_2\\ CO\end{array}{>}CMe{\cdot}CO_2Et$."
2275	1	,, "3-*methyl*-" read "2-*methyl*-."
2275	10	,, "3-*Methyl*-" read "2-*Methyl*."
2275	10	,, " $C_6H_4{<}\begin{array}{c}CHMe\\ CO\end{array}{>}CH_2$" *read* " $C_6H_4{<}\begin{array}{c}CH_2\\ CO\end{array}{>}CHMe$."
2275	11	,, "3-*methyl*-" read "2-*methyl*."

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* From bottom.

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